

Monographs on
Inorganic & Physical Chemistry

CHEMICAL AFFINITY

L. J. HUDLESTON

MONOGRAPHS ON INORGANIC AND PHYSICAL CHEMISTRY

EDITED BY ALEXANDER FINDLAY, M.A., D.Sc., F.I.C.

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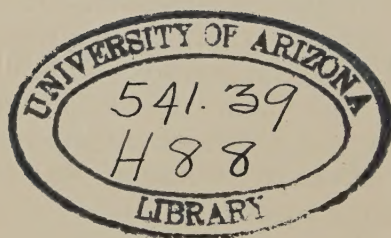
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AUTHOR'S PREFACE.

THE term "monograph" usually implies a detailed and comprehensive exposition of some very limited field for the benefit of advanced students. The subject, "chemical affinity," however, in all its associations is far too large for this, even a comprehensive bibliography would require a greater space. The present work seeks only to develop one aspect of the subject, namely, the use of thermal and equilibria data to assist in the design and control of new problems of reaction. In spite of the increasing attention to thermodynamic methods given in our colleges, I fear that comparatively few young graduates could, for example, discover from the data of Baur that, although the hydrolysis of silicon tetrafluoride by water vapour is increased when the temperature is raised, virtually complete hydrolysis is not to be expected at any temperature. Thus the emphasis has been laid on approximate methods which are useful in application to new problems rather than on precise formulæ which can most accurately represent the data in well-investigated cases.

Thermodynamic methods involve mathematics which, in the words of the immortal Gibbs, "is a language," but which, in this connection, has been given so many dialects that the beginner may well be hopelessly confused. Accordingly, it was thought best to develop the subject from the beginning in consistent terms, even though this involved curtailing the applications. The first two chapters seek to give an exposition of the classical laws of thermodynamics, and to show how the changes of energy are analogous to

chemical reaction, though we are forced to adopt a different treatment owing to the difficulties of analysis.

Roughly, it may be said that the subject has passed through three stages of development. Willard Gibbs laid the fundamental mathematical foundation, the van't Hoff-Nernst school showed how this may be applied to chemical problems on the basis of general, approximate laws, and G. N. Lewis, by the happy introduction of the term "activity," retained these general equations in all their original simplicity, and yet showed how to make them applicable with precision to each specific case. For this reason, and also on account of the large amount of numerical data accumulated by him, the notation of the last-named authority has been adopted here, and the third and fourth chapters are largely devoted to expounding it. But it is in the last chapter, although hardly a quarter of the whole, that the main purpose lies, and if this serves to assist research workers to learn how to survey their problems, to estimate the most favourable conditions for experiment, and to study the possibility of disturbance by side reactions, this purpose will, indeed, have been fulfilled.

In conclusion, it might be pointed out that the methods discussed in the fifth chapter are of almost universal applicability, and it would be hard to think of anything more likely to benefit chemistry as a whole, both academic and industrial, than the foundation of a fully-equipped thermal laboratory in which the necessary data, so sadly deficient at present, might be attained.

I have to thank the authors and publishers of Lewis and Randall's *Thermodynamics and the Free Energy of Chemical Substances* for their kind permission to use their table of free energies which supplies the bulk of the data in the table appended to this volume.

L. J. HUDLESTON.

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ERRATA.

- Page 42, line 29: *for* "2·303 RT" *read* "−2·303 RT."
- „ 60, „ 4: *for* "L" *read* "−L," and *for* "1438" *read* "−1438."
- „ 77, „ 30: *for* " $\beta m^{\eta a}$ " *read* " βm^a ."
- „ 85, „ 26: *for* "97,790" *read* "−97,790."
- „ 89, bottom line: *read as* " $d(\Delta F)/dT = I - a - a \log_e T$," etc.
- „ 91, line 4: *for* "RT" *read* "−RT."
- „ lines 19 and 31: *for* "I" *read* "IT."
- „ 92, line 8: *for* "RT" *read* "−RT."
- „ 3, below table: *read* " $\Delta C_p = -7$."
- „ 102, bottom line: *for* "−32,070" *read* "−37,070."
- „ 104, line 25: *for* "0·2" *read* " $\sqrt{0\cdot2}$ "; *whence* line 26: *read* "8·4" *for* "5·6."
- „ 107, „ 26: *for* "600° C." *read* "625° C."; *whence* line 32: *for* " $\bar{3}\cdot178$ " *read* " $\bar{3}\cdot082$."
- „ 108, „ 8: *for* "68,470" *read* "68,270."
- „ 14: *for* "398" *read* "373"; *whence* bottom line: *read* "K = 11·4."
- „ 111, „ 3: *for* "2AgS" *read* "Ag₂S."
- „ 112, „ 8: *for* "1820" *read* "18,280."
- „ 10: *read* " $S_2(g) + 2H_2(g) = 2H_2S(g)$, $\Delta F^\circ = -33,960$."
- „ 114, „ 4 below table: *for* " $\log_{10} K$ " *read* " $\log_e K$," and *for* "4·576" *read* R.
- „ 116, „ 13: *read* "R has the numerical value, 0·08206."
- „ 125, „ 36: *read* " $\log_{10} K_p = 7\cdot7218$ at 377° K. and 6·0835 at 543° K."; *whence* page 126, line 2: *read* " $(-\Delta H/4\cdot576) = 2019$."
- „ 127, „ 14: *for* "−26,460" *read* "+26,460."
- „ 17: *for* "equation 92" *read* "equation 15B, p. 92."
- „ 128, „ 16: *for* "−15,275" *read* "−15,121."
- „ 131, „ 27: *read* "MgO, $\Delta F^\circ = -137,000$."
- „ 30: *read* " $NH_3(g)$, $\Delta H = -11,000$."

CHAPTER I.

ENERGY AND ITS TRANSFORMATIONS.

THE origin of the term "chemical affinity" must doubtless be ascribed to the very early conception that chemical combination and decomposition were due to the loves and hates of the atoms. When these romantic ideas were replaced by the more prosaic principles of mechanics the term was employed, rather loosely, for the "force" which was supposed to exist between atoms and cause them to combine. But mechanical forces may be modified by leverage or gearing, and in an analogous manner it might be supposed that chemical affinity defined in any such way would be indeterminate and dependent upon the particular mechanism offered to the reaction. On the other hand, chemical reaction is always accompanied by energy changes which are independent of the exact course of the reaction. Many reactions which proceed very readily liberate in the process a large amount of heat, and this led Thomsen and, independently, Berthelot to suggest that the heat liberated might prove to be a quantitative measure of the tendency to react, or chemical affinity. But this cannot be true, because there are many reactions, especially between gases, which take place quite readily and yet are accompanied by an absorption of heat. It was left to van't Hoff to introduce the conceptions, as explained in this chapter, which gave a definite meaning to the term "chemical affinity" such that it could be quantitatively expressed. This also depends upon the transformations of energy which accompany chemical and physical changes, but in a somewhat more complex way than was involved in the crude postulate of Berthelot and Thomsen. It is to be observed that in this treatment it is impossible to distinguish between ordinary chemical reactions such as the formation of water from hydrogen and oxygen and the so-called "physical" processes of melting and volatilisation, so that these latter will be included in the general term.

Thus the changes of energy which always accompany chemical reaction are of hardly less importance to the modern chemist than the material changes themselves. The two are closely connected and show some interesting analogies. Although the laws under which transformations of energy proceed may be studied without reference to any theory of the structure of matter, when the science is called by the forbidding name of "thermodynamics," it is far easier for a chemist to study the subject in the light of the molecular and kinetic theories with which he is familiar, and it is along these lines that the subject will be presented in the present monograph.

Energy, like matter, exists in various forms which may be converted under suitable conditions one into another. But there is an important difference in that it is only the changes of energy which can be measured instead of the absolute amounts. We can withdraw energy from a system and measure quantitatively by how much the energy content has been reduced, but we cannot measure in absolute terms the amount present either before or after the change. This makes the subject essentially comparative and introduces slight difficulties in using numerical values as there has always to be an implied reference state, but provided this is kept well in mind the complication should not prove in the least serious.

Just as the chemist uses a different unit of mass for each substance, the gram-molecule, so the units employed for the measurement of the changes of energy vary with the form under consideration. The simplest mechanical definition of the transference of energy is that of a force exerted through a distance, and if the former is measured in dynes and the latter in centimetres, the product of the two measures the energy transferred in ergs. From this it is seen that a volume change against a pressure also represents a transference of energy, since pressure is force divided by area and volume is length (distance) multiplied by area, and the product of the two must therefore have the same dimensions as before. The usual unit we shall employ for this is the litre-atmosphere, that is, the energy transferred by an expansion of one litre against a constant pressure of one atmosphere. The passage of electricity between two regions at different potentials also measures a transference of energy, the product of the quantity of electricity which has passed (measured in



coulombs) and the difference of potential (in volts) gives the energy transference in joules. The last form of energy transference which need be mentioned is that of heat, where the unit is the calorie (amount of energy which must be added to increase the temperature of one gram of water from 14.5 to 15.5° C.), distinguished from the others by the fact that it is not obtained as the product of two terms. The relation between these units is shown in the following table, the values being taken from *International Critical Tables*, 1926. Four significant figures only are given here and the erg is omitted, being 10^{-7} joules:—

	Joule.	Litre-Atmos.	Calorie.
Joule	1	0.009873	0.2389
Litre-Atmosphere	101.3	1	24.20
Calorie	4.185	0.04131	1

These units serve to measure the transference of energy under different conditions, but the forms in which it can exist may be considered rather differently. They are either kinetic or potential, the latter being postulated to explain the appearance of energy made manifest by transference when certain changes take place. Thus, the existence of potential energy between hydrogen and oxygen is postulated because heat is evolved when the two gases combine. It is the fact that we have no clear conception of the real nature of potential energy which compels us to deal in the main with changes only and prevents absolute measurements.

If a system be taken in some definite state and under given conditions it may be assumed to have associated with it energy in various forms amounting in all to, say, E . If now it be put through a series of changes, ultimately being brought back to exactly its original state and conditions, and if all the energy exchanges between it and the surroundings be measured, gains by the system being reckoned positive and losses negative, the net effect is found to be zero. Consequently, E is said to measure an "intrinsic" property of the system, that is, a property the numerical value of which depends only upon the nature of the system, its state and conditions at the time, and not in any way upon its previous history. To this property the name "total energy" has been given, and it follows from what has been said that, if the system change from state A to state B (change of conditions being included in the term change of state), the difference in total energy depends only upon the two states and

not at all upon the way in which the change is carried out. Moreover, if, for example, x grams of water undergo some specified change, such as being cooled from 20° to 10° , the heat lost will be x times that observed when one gram of water suffers exactly the same change. This is expressed by calling the total energy an "extensive" property, meaning thereby one which, other things being equal, will be proportional to the amount of the system considered. It is thus possible to speak of the specific total energy of a substance, or the total energy per gram, in the same way as one may speak of its specific volume, but with the difference that it is not possible to measure the absolute specific total energy, but only the difference found as between the substance in one state and in another.

All other forms of energy may be transformed and transferred to a calorimeter as heat, exact equivalence being obtained between the energy change observed and the heat produced. The inter-conversion of other forms, e.g. of electrical potential energy into kinetic energy, is not in practice possible without simultaneously transferring some of the original energy into the system and its surroundings as heat, but, if correction be made for this, exact equivalence is found in all these changes too. Consequently, we are led to postulate a law of conservation of energy exactly analogous to that of the conservation of matter and this is usually called the first law of thermodynamics. The evidence for it has here been only roughly sketched, as the theorem presents no difficulty to the mind, but it will be observed that the conception of potential energy is largely introduced to make this law true. Thus we have to expend energy (by exerting a force through a distance) in separating two magnets, and while they remain separated the energy is not apparent. But it may be recovered on allowing the magnets to come together again and is therefore supposed to have been present all the time they were separate in a mysterious form called "magnetic potential energy."

In the same way, when energy is added to a system as heat it must exist in some form, and to this we give the name "thermal energy," but here we have a rather clearer idea, in some cases, of its exact nature. According to the kinetic theory, thermal energy is a jumble of different kinds of energy distributed at random among the molecules *with incessant transformations from one form to another and back again going on all the time*. This is

quite analogous to the state of things ruling in chemical equilibrium. For example, in an equilibrium mixture of hydrogen, iodine and hydrogen iodide, we suppose that there is incessant decomposition of the hydrogen iodide molecules balanced statistically by equally rapid formation from the elements. In fact, equilibrium, whether of matter or energy, is nothing but that distribution which is statistically most probable under the given conditions, and must result whenever continual inter-transformations are freely possible. Thermal energy, then, may consist of any number of forms of energy provided that they are in general equilibrium when the conditions are uniform throughout the system concerned.

It is worth while considering a few cases in detail. The simplest of all is that of a perfect, monatomic gas where the thermal energy consists entirely of the kinetic energy of random rectilinear motion of the molecules. The energy of each molecule is varying from moment to moment as the result of collisions but the average value is supposed to be proportional to, and therefore a measure of, the temperature on the absolute scale. One gram molecule (often called one mole) of gas contains about 6×10^{23} actual molecules, and with such almost inconceivably large numbers the average (and, therefore, the total) energy may remain constant with an accuracy far exceeding that of our most precise measurements in spite of the incessant and wide variation of the value for each molecule considered separately. If we were to make an analysis, by the methods of statistical mechanics, of the actual distribution of energy among the molecules, we should find that it was by no means nearly uniform, but the proportion having, say, 50 per cent. of the average energy at any moment remains statistically constant, and the same for any other chosen value. Measurements of the pressures and volumes of real gases, studying and correcting for their imperfections, show that one gram-molecule of perfect monatomic gas should have a thermal energy content of $1.248 \cdot 10^8 \cdot T$ ergs,¹ where T is the temperature on the absolute scale. Thus the temperature of any system may be defined by allowing a perfect monatomic gas to come into thermal equilibrium with it and then dividing the thermal energy (in ergs) of one gram-molecule of this gas by 1.248×10^8 . When we come to deal with the thermal energy of real substances at very low temperatures (*vide* Chap. V.), we

shall find a great advantage in defining temperature in this way instead of by any reference to the molecular energy of the substances themselves.

For analytical purposes it is convenient to resolve the total thermal energy of a perfect monatomic gas into three parts for the three degrees of freedom which correspond to the three directions at right angles into which the motion is resolved. It has been shown by statistical mechanics that the energy associated with each degree of freedom must be the same. If a perfect diatomic gas be mixed with a monatomic gas, the incessant collisions will produce equilibrium. As a result, the average energy of random translational movement will be the same for both kinds of molecules. But the diatomic molecules are also capable of containing energy of rotational movement which may be resolved into two degrees of freedom corresponding to two possible axes of rotation. Once again it is found that the energy per degree of freedom must be the same, so the total thermal energy of the diatomic gas must be five-thirds that of the monatomic, since it has five instead of three degrees of freedom. Thus its thermal energy will be partly due to the random rectilinear motion of its molecules (in which respect it will contain as much as a monatomic gas), and partly due to rotation of these molecules. Equilibrium will be maintained because there will be continual transformation from rotational to translational energy, and *vice versa*, as a result of collision.

Many real gases show very close agreement with these values for their heat capacity, i.e. the energy required to raise the temperature one degree, provided the temperature is not too low. There is, however, always a potential energy between the molecules which becomes manifest when the gas is cooled to the liquefaction point, but remains very nearly constant at higher temperatures. Owing to the continual collisions there can be no doubt that this potential energy is in equilibrium with the kinetic energy of random movement but apparently the amount does not vary appreciably with temperature once the substance has assumed the gaseous state. The thermal energy of a real gas like helium would therefore be closely represented by a formula of the type, $E_{\text{thermal}} = L + 1.248 \cdot 10^8 \cdot T$ ergs per gram-molecule, where L represents the potential energy which is latent in the system. The unknown total energy, of

course, includes this together with the gravitational potential energy with respect to the earth and heavenly bodies, the kinetic energy of movement through space along with the earth, etc., etc. Its total amount is quite unimportant, since we deal only with changes, and all these other terms are usually kept constant.

A more complicated case is presented by an equilibrium mixture of hydrogen, iodine, and hydrogen iodide (all in the gaseous state), because here there is another form of energy present, chemical potential energy between the molecules. This is in equilibrium with the other forms, since there is continual transformation in the course of collision, but it will no longer be equal to the energy per degree of freedom found for the other forms. Hence it is not possible to write the thermal energy of the system as a linear function of the absolute temperature, for the equilibrium value of this potential energy varies with temperature in a complex way which has to be determined by experiment.

The analysis of the thermal energy of solids and liquids is far more difficult, because the potential energy existing between the molecules, though less than that of gases, varies more with conditions, but the same principle of equilibrium, due to continual interchange between the various forms, applies. It may be noticed that at 0°C . and one atmosphere pressure, ice and water can exist side by side in equilibrium with very different thermal energies per gram, due to water exhibiting a potential energy not present in ice. But it can hardly be doubted that, at the surface, molecules are continually passing from the ice to the water and *vice versa*, i.e. that ice is continually melting and a corresponding quantity of water freezing.

If the distribution of energy throughout a system is not an equilibrium one, it follows that there must be a tendency for transformation or transference to take place until it is so, for equilibrium is simply the most probable distribution. For example, a mixture of hydrogen and iodine vapour at, say, 500°C . has more chemical potential energy than corresponds to equilibrium, and so it will have a tendency to form hydrogen iodide. Some of this potential energy will thereby be liberated and be transformed into energy of random molecular movement, so that the temperature will tend to rise. On the other hand, pure hydrogen iodide at the same temperature would contain too little potential energy for equilibrium, and there would be a tendency

for decomposition to occur, the necessary potential energy being supplied at the expense of the kinetic energy, and the temperature would tend to fall. Such a tendency may not always manifest itself. For example, a mixture of hydrogen and oxygen at ordinary temperatures is not in equilibrium, but will remain unchanged for an indefinite time. The tendency to change is, however, still there, as may be seen by adding a little platinum black (which does not alter the essential energy distribution) when combination immediately begins. On the other hand, no system in equilibrium will exhibit any tendency to further change so long as the conditions are unaltered. Thus an equilibrium mixture of hydrogen, hydrogen iodide, and iodine vapour will not of itself undergo any statistical change of composition, although individual molecules are decomposing and forming. All this may be formulated as a second fundamental law in the statement: in an isolated system (that is, one which cannot exchange energy with its surroundings) only such changes can take place as tend to bring the energy into general equilibrium.

In so far as energy is not in equilibrium, it is said to be "available" because the tendency it has to get into equilibrium is available to produce change. Thermal energy, in a system which is at a uniform temperature throughout, is not available, as we have seen. When, however, uniformity of temperature has not been established there is a natural tendency to change, and in such a case some of the thermal energy (or energy of random molecular movement and such other forms as are in equilibrium with this) is available. This will be considered in the next chapter. Here we shall consider only systems where the random molecular movement has established thorough equilibrium throughout and where, therefore, the temperature is the same at all parts.

Some forms of energy are incapable of existing in general equilibrium such as we have discussed, one such form being gravitational potential energy. Any free weight will fall as far as circumstances allow, and, when it is stopped, energy, equal to the amount of potential energy lost, will be added to the random energy of motion of the molecules of itself and its surroundings. Here, again, we see the action of probability. As far as the law of conservation is concerned, there is nothing to

prevent this extra energy all being localised again as movement of the molecules in a specific direction at the base of the weight, throwing it back again to its original position ; but this does not happen, because it would be too improbable that the extra energy should ever be so localised and directed at any given moment. The energy which, when in its "available" form, was concentrated has been dissipated and shared among millions of particles, and it is too improbable that it should ever again become concentrated of its own accord. Thus, when energy which was concentrated in an available form is brought by some change into general equilibrium, it is said to be "degraded." Our second law, therefore, takes the form that "all changes involve the degradation of energy if everything affected be taken into account, for, when this is done, we have what is, or might be, an isolated system."

Electrical potential energy will also always tend to disappear completely, electricity always flowing from a region of higher to one of lower potential if a suitable path is provided and no external influences are at work. These two forms, gravitational and electrical potential energy are therefore completely available.

Though available energy is never produced spontaneously from energy which is in general equilibrium, it is possible to link such forms together in such a manner that, while available energy is lost in one part of the system, it is gained in another. Thus two weights may be connected by a cord over a pulley so that as one falls the other is raised. It will be the heavier weight which falls (with a simple pulley), and its loss of available (gravitational potential) energy will be the same as if it had fallen freely, but now only a portion of this will be degraded into thermal energy, the remainder being transferred as available (gravitational potential) energy to the weight which is raised. When available energy is thus transferred from one part of a system to another the first is said to "do work" on the second.

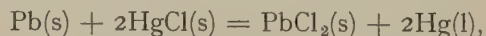
By the law of conservation of energy, the loss of potential energy of the first weight must equal the gain in potential energy of the second together with the heat (thermal energy) produced. This last term measures the degradation of energy which has occurred in the system as a whole, and by our second law the first weight will not fall at all unless some energy is thereby degraded. In theory the least amount of degradation would

make the process a possible one, and even in practice we can get the falling weight to raise one of very nearly equal mass. If the two weights were exactly equal there would be no tendency for any movement, because it would not result in any degradation of energy, as all the available (potential) energy lost by the first weight would be transferred to the second. Conversely, if we just balance the tendency of the first weight to fall by suitably connecting it with a second weight, thus securing equilibrium, we can measure the loss of available energy the first weight would suffer in its fall by the amount the second would gain *if* the change took place under these conditions. Although no such change would actually take place, we can calculate what would happen *if* it did from the mass of the second weight necessary to establish equilibrium and the height through which it would be raised by the fall of the first. In so simple a case, there is no need for such a procedure, but the same principle may be employed where the degradation of energy is not of a form that can be readily analysed, but may equally simply be kept in equilibrium. The loss of available energy of the process which we wish to discover (corresponding to the loss of potential energy of the first weight) may be calculated from the available energy which would be transferred to some simpler system (corresponding to the potential energy acquired by the second weight), if the process had taken place under equilibrium conditions, a value which may often be calculated although no change under such conditions will actually occur.

The use of this principle is perhaps best seen in an example. Suppose we set up the cell,



in which the chloride solution in contact with each electrode is saturated with the corresponding salt. On connecting the electrodes by a wire electricity will pass along the wire and a change will take place in the cell expressed by the equation



and for the number of gram-molecules indicated by the equation 2 faradays of electricity would pass through the cell from the

* The state of the substance, solid, liquid, or gaseous, is indicated by the letter within the brackets.

negative to the positive electrode. If, instead of connecting the electrodes with a simple wire, we connect them with a source of counter-electromotive force, we can resist the change, stop it, or reverse it at will, according to the magnitude of the counter-electromotive force. If the cell be kept at 25° , the counter-electromotive force which will just stop the change and maintain equilibrium is 0.5357 volt.² If, now, the change be *imagined* to take place against this equilibrium counter-potential, the cell would produce electrical potential energy in the counter-force system amounting to 2×0.5357 volt faradays = 24,760 cal.* But we have seen that electrical potential energy is entirely available, since it tends to be completely transformed into thermal energy, as has already been discussed. Consequently, its appearance must be due to transference of available energy from the cell and, as equilibrium conditions were assumed in the calculation, it measures quantitatively the amount of available energy which must be degraded when the same chemical change takes place freely. This is exactly analogous to our previous case of the two weights in equilibrium, where the increase of potential energy of the weight which was raised measured quantitatively the decrease in the available energy of the weight which fell.

It is of the essence of true equilibrium that if the counter-force (the second weight or the counter-electromotive force in our examples) be the least fraction too great, the process takes place in the reverse direction (the first weight is raised or mercurous chloride is formed and lead deposited), and if it be the least fraction too little the change originally discussed will occur. The transformation under equilibrium conditions therefore constitutes, in either direction, the theoretical limit of spontaneous change. Moreover, if it be imagined to take place first in one direction and then in the other until the original conditions are exactly restored, all under equilibrium conditions, there will be absolutely no change in the condition of anything as a result of the combined process, for energy is not degraded at any time but merely transferred from one part of the combined system to another and back again. Such changes (under equilibrium conditions) are therefore called "reversible" in the thermo-

* 1 faraday = 96,500 coulombs.¹

dynamic sense, because everything can be reversed and restored without change anywhere. Real changes are always irreversible, involving some degradation of available energy somewhere, but the imaginary reversible change would involve only transference of available energy without degradation. The amount of energy so transferred can, however, be calculated from equilibrium conditions, although the change would not really take place at all where these exist. Thinking, now, of the separate parts of the complex system, the cell for example and the counter potential system, the amount of available energy transferred from the one to the other is the work done by the first on the second, and this would reach its maximum value if the change were arranged to take place reversibly. It will be noticed that the possibility of calculating this comes from the fact that energy transferred as work can always be expressed as the product of two factors, one an intensity factor, corresponding to a force and determinable from equilibrium conditions, and the other a capacity factor, corresponding to a distance, which is the same whether the change takes place reversibly or not. Thus, when a weight is raised, the capacity factor is the height through which it is raised, which is independent of whether it is lifted by the falling of an equal or of a greater weight, whilst the intensity factor is the weight (a force), the maximum value which can be lifted being determined from equilibrium conditions. Similarly, the formation of one gram-molecule of lead chloride and two gram-molecules of mercury from one gram-molecule of lead and two gram-molecules of mercurous chloride, when it takes place in the cell described, requires the passage of two faradays (193,000 coulombs) of electricity whatever the counter-electromotive force may be, and the product of this and the equilibrium counter-electromotive force gives the maximum work of the change.

We may thus summarise the ideas put forward. In an isolated system change can occur only in so far as the energy is not already in general equilibrium; the system is then said to have "available" energy. If an isolated system can change, and therefore possesses available energy, it could, if not isolated but suitably connected, do work on a second system by transformation and transference of some of its available energy. The maximum work which could conceivably be done on the

second system during any specified change in the first is done when the change is carried out reversibly (i.e. under equilibrium conditions), when all the decrease of available energy associated with the change in the first system is transformed into work in the second. It is possible to calculate what this would be, although no actual change could take place at all under equilibrium conditions, since no energy is degraded. It may be observed that the more nearly equilibrium conditions are approached, the more slowly does a change occur, so that the imaginary reversible process would take infinite time.

A special case of great importance must now be considered in detail. Imagine a vessel divided into two parts by a partition, one part being filled with perfect gas and the other evacuated. The energy of the gaseous part, considered by itself, is in general equilibrium, and the same must be true of the evacuated part considered by itself, because it contains no energy at all of the kind we are considering. The two parts are not, however, in equilibrium with each other, so the system as a whole is not in general equilibrium, and a change will occur spontaneously if suitable mechanism is provided, such as a hole in the partition. Hence, there must be available energy in the system as a whole, and energy is degraded when a gas expands into a vacuum. As required by the first law, the total energy is unaltered by the change, and it is entirely thermal both before and after, but the degradation arises from the changed distribution in space, this being just as important as its distribution between the various possible forms. Purists might prefer the term "availability" of energy, but, as the system may be used to do work, i.e. to produce a form of energy which is entirely available, the distinction seems unnecessary.

Work may be obtained from the system by making the vessel cylindrical and the partition a gas-tight piston (supposed frictionless for convenience) so connected that if it be pushed back through the vacuum it raises a weight. The tendency of the gas to expand and fill the cylinder uniformly can then be employed to do work by raising the weight, provided it be sufficiently light. If the weight is too heavy, it will reverse the process and do work on the gas by compressing it. Equilibrium can be attained by the choice of a suitable weight, but this varies with the position of the piston. It would, however, be easy to devise

a system of gearing such that the force of the weight was continually reduced as the piston was raised, just sufficiently to ensure equilibrium throughout the stroke.

At first sight it might appear that the potential energy of the weight entered into general equilibrium with the thermal energy of the gas, but this is not so, for the piston is not exposed to random bombardment by the gas molecules, but only to bombardment on one side, so that every possible molecular impact has at least a component in the same direction. In other words, it is because the vacuous space above and the gas-filled space below are not in equilibrium that the piston is able to support the weight. Consequently, the potential energy of the weight does not enter into *general* equilibrium, but establishes a "special" equilibrium with the available energy of the system due to the non-uniform distribution of the gas.

With such an arrangement, we can calculate the work done (on the weight) during a reversible expansion if we know how the pressure of the gas varies with the volume; for work done is measured by the product of the pressure into the volume change through which it is exerted. When the pressure is continually decreasing as the volume is increased we must employ the calculus. During the infinitesimal increase of volume, dV , the pressure remains constant and the work done is $p \cdot dV$, and for a finite expansion from volume V_1 to V_2 the work done is given by the integral $\int_{V_1}^{V_2} p \cdot dV$. This can be evaluated only if we know the relation between p and V throughout the change.

If no other energy changes took place at the same time, the only possible source of the energy added to the weight would be the thermal energy of the gas, and we should have the additional complication that the temperature would be falling throughout the operation, a case which is best deferred until later. This is avoided by immersing the cylinder in a constant temperature bath, such as a mixture of ice and water at 0°C . During the reversible change, which takes place infinitely slowly, there will be no finite difference in temperature between the gas and the bath, and, therefore, the heat passes under equilibrium conditions and there is no degradation of energy. Further, no available energy is transferred between the two, so the bath

does not affect the maximum work obtainable from the system, except in so far as it defines the conditions of the change, that the temperature shall not alter. It is therefore unnecessary to consider the nature of the bath.

With this restriction as to the temperature being constant and assuming that we are dealing with one gram-molecule of gas, $p = RT/V$,* the integral required is $RT \log_e (V_2/V_1)$. This, then, is the decrease in available energy when one gram-molecule of perfect gas occupying a volume V_1 expands at constant temperature into a vacuum until it occupies a volume V_2 . If the process were allowed to take place without doing any work at all, this amount of available energy would be degraded. The degradation does not involve any transformation of energy, but merely a different distribution in space, so, if it took place freely, there would be no transference of energy between it and the bath. That degradation really has taken place is seen from the fact that in order to restore the original condition by compressing it from V_2 to V_1 again, leaving a vacuum above, available energy, such as the potential of a weight, must be used up, the least amount sufficing for the work being that employed in a reversible compression, namely, $RT \log_e (V_2/V_1)$.

It may be emphasised once more that if the change is carried out reversibly and then restored, also reversibly, the energy relations of everything concerned are left unaltered, since the thermal energy lost by the bath during the expansion equals the gain of potential energy of the weight, and the same weight, moving down the same path, restores the old conditions, yielding just exactly the extra energy it previously gained back to the bath. But, to carry out the process and its restoration in reality, the weight which was raised would have to be lighter, and the weight which falls during the restoration would have to be heavier, than the one concerned in the reversible change, hence the heat lost by the bath during the expansion would be less than that gained during the compression, and the net result, taking everything affected into account, would be that some potential energy had been degraded into thermal energy, though the conditions as far as the gas and vacuum were concerned would be exactly restored.

* Numerically $^1 R = 0.08206$ litre-atmospheres per degree = 1.9874 cals. per degree = 8.315 joules per degree.

It may be noticed that our conception of available energy always refers implicitly to some final condition of equilibrium, and this, in turn, depends upon the conditions imposed. Thus, in the example given above, we say that equilibrium is reached when the space is uniformly filled with gas, but that is true only so long as the condition that the gas remains in the cylinder is fulfilled. If the cylinder were to burst, the gas could, and would, disperse still further, showing that there was still available energy present—with reference to some new condition of equilibrium. Hence, we are not really dealing with absolute measurements but with changes in available energy associated with definite physical and chemical changes which must be carefully specified. Thus, if the expansion of gas into a vacuum were conducted reversibly, but without any thermal energy reaching the gas from any source (a problem considered later), the decrease in the available energy of the system will not be that given above, because we should not be considering the same change as before where the temperature was unaltered. To describe a change accurately the initial and final conditions must be clearly defined.

An important theorem for future use is that the maximum work that can be obtained from any specified *isothermal* process is independent of the mechanism of the process (though, of course, it must be conducted reversibly to obtain maximum work). This follows directly from what has been said, since the maximum work obtainable is equal to the decrease in the available energy resulting from the change, and from our analysis of the energy relationships we know that this is quite definite and depends only on the initial and final states. The importance of the theorem, however, justifies an illustration and some further discussion.

We may take as an example the expansion of one gram-molecule of hydrogen from a pressure p_1 to a pressure p_2 at constant temperature. Assuming that the gas is perfect, we may carry out the operation as just described, when the work done will be equal to $RT \log_e (V_2/V_1)$. Alternatively, we may have two platinum electrodes dipping in the same solution of acid and surrounded with hydrogen kept mechanically at a pressure p_1 round the first, and at p_2 round the second. On connecting the electrodes, hydrogen will pass into solution at the first, and will

be evolved at the second. If one gram-molecule of gas be thus transferred, 2 faradays of electricity will pass, and if a counter electromotive force, E , oppose the change at the equilibrium value, the process will be carried out reversibly and do work to the extent of $2 \times 96500 \times E$ joules. At the same time, the mechanism for keeping the pressure constant around the first electrode does work on the gas equal to $p_1 V_1 = RT$, since the pressure p_1 is exerted through the volume V_1 due to the disappearance of one gram-molecule of the gas. Similarly, at the other electrode the gas does work $p_2 V_2 = RT$ on the pressure system. These two effects could be made to neutralise each other, leaving the electrical work as the net result. Consequently, by our theorem, $2 \times 96500 \times E$ joules $= RT \log_e (V_2/V_1)$ cals. We may imagine the process carried out by one method, say by direct expansion against a weight, and restored by the other. The energy relations of the gas will then be exactly what they were at the start, and if the maximum work by the first method were greater than that by the second, the surroundings would contain more available energy than they had before. But this could have come only from the thermal energy of the constant temperature bath (which must have been present to assure constant temperature), and so we should have a case of thermal energy spontaneously changing into available energy, i.e. the system as a whole would have spontaneously changed its distribution of energy for a less probable one. This is contrary to our second law. Similarly, by reversing the methods employed to bring about the change and restore it, we prove that the electrical method cannot yield more work than the expansion against a weight, i.e. the two methods give identical values for the maximum work obtainable from the change.

This illustrates the significance of another method of stating the second law, namely, it is not possible for heat (thermal energy) to be converted into work at constant temperature without compensation. When gas expanded isothermally into a vacuum it was possible to convert heat into work, the compensation being provided by the change of the distribution of the energy of the gas in space, but in restoring that change the compensation is foregone and at least as much work must be employed for the restoration as was produced by the original expansion.

So long as we are dealing only with isothermal changes the maximum work obtainable from a given process is perfectly definite and equal to the decrease in the available energy of the system. Since all spontaneous changes involve a degradation of energy, no change can take place in an isolated system unless it could do work if the system were not isolated but suitably connected to some other. Therefore, van't Hoff employed the maximum work obtainable from an isothermal process as a measure of the chemical affinity of the change. If this is to represent the innate tendency to react care must be taken that the initial conditions (temperature, pressure, and concentration) are not altered in the course of the change. For example, if we wish to express the tendency for water vapour to pass from a region where the pressure is p_1 to that where it is p_2 by the maximum work obtainable from the passage of one gram-molecule, we must not allow the process to lower p_1 or raise p_2 . Mechanical compensation for the actual transport of matter must be provided and allowed for in the calculation.

It is usual to work at constant pressure when, if there is any volume change, work equal to $p \cdot \Delta V$ (where ΔV is the increase in volume) is done by the chemical system against the atmosphere, and it is convenient to separate this from any other work, called extraneous work, which may also be done. We may then formulate our first law in the equation

$$Q = \Delta E + \int_1^2 p \cdot dV + W \quad . \quad . \quad . \quad (1)$$

where Q is the energy which passes in as heat (if passed out Q is numerically negative), ΔE is the increase of total energy of the system, the integral denotes the work done by the system against the surrounding pressure (which will be numerically negative if the surrounding pressure does work on the system), and W denotes any extraneous work done by the system (which also will be negative if work is done on the system by some other system). This equation will be true for any change whatever, and may be expressed thus: The energy which passes in as heat will be equal to the increased energy of the system resulting from the change together with any energy which escapes as work of any kind, net effects being referred to in each case.

For the special case that the pressure is constant throughout the change, equation (1) becomes

$$(Q = \Delta E + p \cdot \Delta V + W)_{p, \text{ const.}} \quad \cdot \quad \cdot \quad \cdot \quad (1A)$$

If we are considering a reversible change, it is well to remind ourselves of the fact by adding the suffix *r* to *Q* and *W*. As we have seen, if a process is not conducted reversibly *Q* and *W* are indeterminate until we know exactly how the process was carried out, but for any specified *isothermal* change, *Q_r* and *W_r* are quite definite.

A complex system consisting of a special chemical system in equilibrium with a constant temperature bath and constant pressure apparatus (the atmosphere) will change only if some available energy is degraded and the amount of this is equal to the maximum work that could be obtained if the system were connected suitably to some mechanism which could oppose and reverse the change. Since equilibrium exists as regards temperature and pressure, no degradation of energy is possible as regards the interchange of energy with the bath and atmosphere, so the maximum extraneous work obtainable from the change is a measure of the degradation of energy (occurring in the chemical system) when the change takes place freely under these conditions, and, therefore, constitutes a measure of the chemical affinity under conditions of constant temperature and pressure. If *W_r* is positive, then energy would be degraded if the reaction took place freely at constant temperature and pressure, and the change would be possible. If *W_r* is negative, work would have to be done, i.e. energy in some other system degraded, in order to bring the change about, and it could not take place spontaneously. If *W_r* is zero, then the initial and final states are in equilibrium. The numerical values of the work done are proportional to the amount of substance undergoing the change, and the chemical affinity must therefore be measured by the maximum work resulting from the change affecting the amount of substance indicated by the equation. Thus, for the reaction $\text{Pb(s)} + 2\text{HgCl(s)} = \text{PbCl}_2\text{(s)} + 2\text{Hg(l)}$, the work must be calculated for the formation of one gram-molecule of lead chloride and two gram-molecules of mercury from two gram-molecules of mercurous chloride and one gram-molecule of lead, involving the passage of two faradays of

electricity if the process is arranged to take place in a galvanic cell. As has been shown (p. 11), the chemical affinity of this is 24,760 cals., and if the reaction had been written



the equilibrium potential would be the same, but only one faraday would pass, and the chemical affinity would be half as much.

Note also that, owing to the little-known action of chemical resistance, it does not always follow that a reaction will take place because there is a positive chemical affinity. Thus, hydrogen and oxygen can exist together side by side at room temperature, although there is a great chemical affinity urging them to react. The presence of a catalyst will, however, make this affinity apparent.

CHAPTER II.

ENTROPY.

If two molecules of a perfect gas collide, the total kinetic energy of the two together must, by the first law, remain unchanged, but, in general, there will be some transference, one molecule gaining energy at the expense of the other. If one, A, initially had more energy than the other, B, it does not follow that it will necessarily be A which loses and B which gains. Which way it is depends largely on the angle of impact, but it may be shown that it is more probable that energy will be lost by that molecule which originally had most. Consequently, when two gases at different temperatures are mixed, energy will be lost on the whole by the molecules of the gas originally at the higher temperature and gained by the others, for, with the enormous numbers involved, probability assumes the force of certainty. Thus thermal energy spontaneously passes from a region of higher, to one of lower, temperature, and this could be shown to be a perfectly general conclusion by following out the equilibria involved according to our definition of temperature. This is unnecessary, as the fact is so well established empirically, and the only object of introducing the analysis is to show that the result is purely a consequence of the law of probability applied to large numbers. Thermal energy and temperature (as defined in accordance with the kinetic theory) are essentially statistical conceptions, and it is unsafe to apply them to a system of a very few molecules.

When thermal energy passes as such from one system to another the first is said to give heat to the second whether it remains there in the same form or is converted into work, as in the reversible expansion of a gas. Heat is therefore not a property but a form of passage of energy. Nevertheless, it is convenient to denote the passage of an infinitesimal quantity of heat by dQ as no ambiguity is thereby introduced.

The heat which must be absorbed by one gram-molecule of a substance in order to raise the temperature by one degree is called the molecular heat capacity of the substance and, from what has just been stated, it is obvious that its value will depend upon conditions, e.g. whether the volume is kept constant or not. In the case of a perfect gas the heat capacity at constant volume is merely the increase in thermal energy per degree, which we have seen to be, for any one gas, a constant, independent of both temperature and volume and determined entirely by the number of degrees of freedom of the molecules. It is denoted by C_v . If the pressure, instead of the volume, be kept constant, not only will the thermal energy have to be increased by the same amount, but also heat will be required to supply the energy transferred to the atmosphere as work, $p \cdot \Delta V$, as a result of the increase of volume, ΔV , against the constant pressure, p . Since the gas is perfect, for each gram-molecule $pV_1 = RT_1$ and $pV_2 = RT_2$. But for a rise of one degree, $T_2 = T_1 + 1$ and $p(V_2 - V_1) = R$. Consequently, the molecular heat capacity of a perfect gas at constant pressure, $C_p = C_v + R$. The ratio between these two heat capacities is easily determined in any actual case (e.g. by the method of Kundt), and is usually denoted by the symbol

$$\gamma = C_p/C_v = (C_v + R)/C_v.$$

In what follows we shall require to know the relation holding between the pressure and volume when a perfect gas expands into a vacuum reversibly and adiabatically, that is, without exchanging any heat with its surroundings. By differentiating the general equation, $pV = RT$, we obtain $p \cdot dV + V \cdot dp = R \cdot dT$. But for a reversible expansion $p \cdot dV$ is the work done against the counter-pressure apparatus, and since there is no other source of energy, it is provided at the expense of the thermal energy of the gas, so $p \cdot dV = -C_v \cdot dT$, the minus sign indicating that the temperature falls and the gas loses thermal energy. Substituting this in the last equation, $V \cdot dp = (C_v + R)dT$, and further substituting $V = RT/p$, we obtain $dp/p = (C_v + R)dT/RT$ or

$$d \log_e p = \frac{(C_v + R)}{R} d \log_e T$$

remembering that $(C_v + R)/C_v = \gamma$ and $R/C_v = \gamma - 1$, multiply through by the latter and,

$$(\gamma - 1)d \log_e p = \gamma d \log_e T = \gamma d \log_e (pV/R)$$

on integrating

$$\gamma \log_e (pV/R) = (\gamma - 1) \log_e p + \log_e k,$$

where $\log_e k$ is a constant of integration, hence $p^\gamma V^\gamma = kR^\gamma p^{\gamma-1}$ or $pV^\gamma = \text{a constant } (R^\gamma k)$.

Returning to the question of heat passing from regions of higher, to those of lower temperature, since this is a spontaneous change, it must involve the degradation of energy. The amount may be determined by the following method, due to Carnot: Let one gram-molecule of perfect gas, occupying initially a volume V_1 at pressure p_1 , expand isothermally and reversibly to a volume V_2 at which the pressure is p_2 , the necessary energy being supplied from a constant temperature bath at T_1 . The heat absorbed from the bath, Q_1 , is equal to the work done on the counter-pressure apparatus, $RT_1 \log_e (V_2/V_1)$. Next let the gas expand adiabatically and reversibly to a volume V_3 , when the temperature and pressure are, respectively, T_2 and p_3 . The work done against the counter-pressure apparatus will be equal to the thermal energy lost by the gas, $C_v(T_1 - T_2)$. Follow this by compressing the gas isothermally and reversibly to a chosen volume V_4 , when the pressure will be p_4 . The energy expended on the gas, $RT_2 \log_e (V_3/V_4)$, will appear as heat in the necessary constant temperature bath at T_2 , and may be denoted by Q_2 . The volume V_4 is so chosen that a further reversible adiabatic compression will exactly restore the original condition of the gas. For this purpose, work will be required equal to the gain of thermal energy of the gas, $C_v(T_1 - T_2)$. All terms have been written so as to give positive numbers, the direction of the passage of the energy being indicated in the context instead of by sign. The whole series of operations constitutes, for the gas, what is called a "reversible cycle," since all changes were carried out reversibly and the final state exactly restores the original conditions. Therefore, the total energy is unaltered and as much has been removed at various stages as has been added in others. Hence,

$$Q_1 + RT_2 \log_e (V_3/V_4) + C_v(T_1 - T_2) = RT_1 \log_e (V_2/V_1) + C_v(T_1 - T_2) + Q_2.$$

This equation is simplified by the fact that $V_2/V_1 = V_3/V_4$, which is proved as follows:—

Since pV^γ is constant during an adiabatic change,

$$p_2V_2^\gamma = p_3V_3^\gamma \quad \text{and} \quad p_1V_1^\gamma = p_4V_4^\gamma.$$

On dividing the first of these equalities by the second and noting

that $p_1V_1 = RT_1 = p_2V_2$, whence $p_2/p_1 = V_1/V_2$,
 while $p_3V_3 = RT_2 = p_4V_4$, whence $p_3/p_4 = V_4/V_3$,
 we obtain $V_2^{\gamma-1}/V_1^{\gamma-1} = V_3^{\gamma-1}/V_4^{\gamma-1}$ or $V_2/V_1 = V_3/V_4$.

Therefore, the energy equation for the Carnot's cycle simplifies to

$$Q_1 - Q_2 = R(T_1 - T_2) \log_e (V_2/V_1)$$

which shows the amount of thermal energy which has been transformed into available energy in the counter-pressure apparatus. The proportion of heat absorbed at the higher temperature which has been so transformed is given by dividing the above equation by $Q_1 = RT_1 \log_e (V_2/V_1)$, when $(Q_1 - Q_2)/Q_1 = (T_1 - T_2)/T_1$.

Taking account of everything affected, the change consists in the transference of thermal energy from the bath at T_1 to that at T_2 , with the simultaneous transformation of as much as possible (since all changes were effected reversibly) into work. The choice of a perfect gas for the working substance necessary to conduct the process reversibly was dictated by the simplicity of the energy relations during the various steps, but any other material would afford the same result, since no ultimate change in the working substance is involved. Thus, the degradation of energy which results when Q_1 units of thermal energy pass from a region at T_1 to one at T_2 is $Q_1(T_1 - T_2)/T_1$.

It is convenient to pause here and summarise the kinds of degradation of energy which have been discussed. There are three types:—

- (a) The transformation of forms of energy which are completely available (e.g. gravitational potential energy).
- (b) The transference of energy in space from a non-equilibrium to an equilibrium distribution (which does not necessarily involve uniform distribution, cf. water and ice at 0°); and

- (c) The transfer of thermal energy from a region of higher to one of lower temperature. In the last two cases we are dealing rather with the "availability" of energy than with any special form, and the analogy with chemical reaction with which we started is rather forced, being dependent on the possibility of their theoretical conversion into case (a) by means of the reversible change. But the underlying principle of the attainment of equilibrium remains perfectly valid, and much of our difficulty lies in the impossibility of an adequate analysis of energy.

Whenever temperature changes arise in the course of an operation, the system under consideration is liable to act as the medium for converting into work some of the decrease in available energy resulting from heat transference. Consequently, the maximum work obtainable from a process which is not carried out isothermally does not correspond to some change in the available energy of the system itself. For instance, in the cycle just described, work was obtained although the system, the gas, was restored to its original state and therefore had its available energy unchanged. But, by rearranging the equation, $Q_1 - Q_2 = Q_1(T_1 - T_2)/T_1$, we obtain $Q_1/T_1 = Q_2/T_2$. Thus, reckoning heat absorbed as positive and heat evolved as negative, we find in this particular case that $\Sigma(Q/T) = 0$. This suggests a generalisation which may be traced out in the following steps. Consider first a complex cycle consisting only of consecutive reversible isothermal and reversible adiabatic processes, such as is represented on the $V - T$ diagram in Fig. 1. Isothermal changes are there represented by horizontal straight lines, and in passing from left to right we may postulate that heat is absorbed, whilst, conversely, on passing from right to left heat is evolved. The oblique lines (which would not really be straight, but are so shown for simplicity) represent adiabatic changes in which no heat passes at all. If the letters shown represent the values of Q/T for each isothermal,

$$\Sigma(Q/T) = a + b + c - d - e + f.$$

But, by adding the dotted lines (for which the letters have the same significance), we have figured three Carnot's cycles and, from what has been said above,

$$a - g = 0, f + g + b - e - h = 0, \text{ and } h + c - d = 0.$$

Adding these three equations together,

$$a + b + c - d - e + f = 0 = \Sigma(Q/T).$$

By extending this form of proof, it would be easy to show that any cyclic process consisting solely of reversible isothermal and adiabatic processes $\Sigma(Q/T) = 0$. But any reversible cyclic process whatsoever can be resolved into a series, infinite if necessary, of such changes, and, therefore, for all reversible cycles

$\int_1^1 dQ_r/T = 0$ (where the identical limits of integration denote that a cycle is concerned and the suffix r is added to remind us

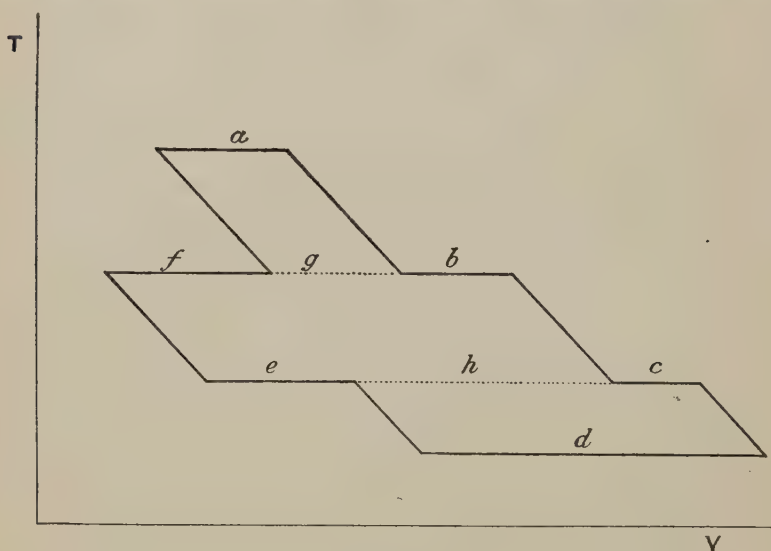


FIG. 1.

that we are dealing with reversible processes only). We may divide the integral into two parts, a reversible change from state I. to state II., followed by a reversible restoration from state II. to state I. again, and

$$\int_1^2 dQ_r/T + \int_2^1 dQ_r/T = 0 \text{ or } \int_1^2 dQ_r/T = \int_2^1 -dQ_r/T.$$

This can be true only if each term separately has a constant value depending only upon states I. and II., which is independent of the path by which the change was made, provided that it is reversible. Consequently, either of these terms defines the

change in some intrinsic property of the system to which we give the name "entropy" and the symbol S . That entropy is also an extensive property follows from the fact that the heat absorbed during any specified change is proportional to the amount of material undergoing the change. As with total or available energy, it is not possible to determine the absolute entropy of any system, although we can measure entropy changes. Indeed, entropy corresponds very closely to available energy except that, with the latter, we have so far been able to measure changes only when they occur at constant temperature, whilst with the former the effect of temperature variation can be taken into account. Changes in either are measured by means of the calculated energy changes occurring during the theoretical reversible process, but are the same, for the same change, whether it takes place reversibly or not.

This last point is so important that it might be well to emphasise it by further discussion. If a system change from state I. to state II., we define the increase in entropy by

$$\Delta S = \int_1^2 dQ_r/T = \int_2^1 -dQ_r/T,$$

where the first integral is that of the heat absorbed divided by the temperature at which it was absorbed during the change when conducted reversibly, and the second is that of the heat evolved (indicated by the negative sign) divided by the temperature at which it was evolved during the reversible restoration of the change. It is quite clear that, for any specified change, the second term, dealing with the restoration, is unaffected by the way in which the original change was carried out. As an example, we may take the case of a weight falling until checked by a string. The former potential energy of the weight is converted into thermal energy when the fall is arrested, and this would remain in the weight if the string be supposed to have no heat capacity and if losses to the surroundings are prevented. The weight, therefore, has as much energy as before, but some potential energy has been degraded. The change can be restored only by introducing some available energy from some outside force, e.g. from the fall of some other weight, but if this alone were done, the final condition of the weight would not be the same as at first, for the extra thermal energy would still be there.

To restore the process exactly, this amount of thermal energy would have to be removed. If the restoration be reversible the available energy added would be that lost in the fall, and a corresponding amount of thermal energy would have to be removed. This is perfectly general. If any change takes place in an isolated system, the total energy is unaltered, but some available energy is degraded. The only way of restoring the change is to break down the isolation and replace the available energy by transference from some external source. But this alone would increase the energy content of the system, and so, to restore the old conditions exactly, thermal energy would have to be removed, i.e. heat would be evolved during the restoration, whether conducted reversibly or not. But the integral of the heat evolved during the reversible restoration divided by the temperature at which it was evolved gives the entropy increase of the original change by definition, and we see that this must be positive. Hence follows the most important form of expression of the second law, that any change in an isolated system increases the total entropy, or, "entropy tends to a maximum."

Since entropy is an intrinsic and extensive property, we may divide up the entropy of a system into that of its various parts, and it must not be thought that the entropy of each part must increase during a change in an isolated system. In fact, we shall frequently meet with cases where one part of a system has its entropy decreased during a spontaneous change, but if everything affected is taken into account (when we have the equivalent of an isolated system), the total entropy must necessarily increase, a law which, when its derivation is followed, springs from the law of probability, and is, therefore, strictly applicable only to systems containing a very large number of parts.

A reversible change takes place under equilibrium conditions, and involves no degradation of energy. Consequently, it could be restored, also reversibly, without drawing on any external source of available energy and therefore, no heat would have to be removed as compensation during the restoration. Hence the entropy is unchanged in this case. Some mechanical changes, such as the interchange of energy following the collision of molecules, are of this type, but they do not constitute processes in the statistical sense, and the reversible changes

we have considered are imaginary, constituting the limiting case of spontaneous change, when the entropy is unaltered.

The application of these considerations to a chemical problem is best seen by an example, for which we shall take the case of the combination of two gram-molecules of hydrogen with one of oxygen at 25° C. and one atmosphere pressure. If this takes place freely, say under the influence of a catalyst, in a system consisting of the chemicals, the atmosphere and a constant temperature bath, the latter will receive 137,000 cal.³ of energy as heat. The origin of this energy is threefold. The smallest part comes from the fact that there will have been a reduction in volume of the chemical system of about 73 litres, and the pressure of the atmosphere acting through this change of volume produces 1780 cal. A second part comes from the degradation of the chemical potential energy which was present before the combination, and a third from the fact that the chemical system in the form of liquid water contains less thermal energy at the same temperature than it does in the form of the mixed gases. The degradation involved may be measured from the work obtainable by carrying out the same change (as far as the chemical system is concerned) reversibly, and this could be calculated from the equilibrium electromotive force of a cell having hydrogen and oxygen electrodes dipping in pure water as electrolyte. This has not yet been measured directly because, so far, no reversible oxygen electrode has been prepared, but the difficulties are quite foreign to the subject of the present argument, and may, indeed, be overcome some day. They may therefore be neglected here, for we know quite certainly, from indirect methods to be studied later, that the value would be 1.227 volts,* if incidental practical troubles were overcome. To conduct the process reversibly the cell



would have to be connected to an external electrical system such that the portion connected to the oxygen electrode had a potential 1.227 volts above that connected to the hydrogen electrode, and the whole would have to be immersed in a constant temperature bath. For the reaction



* See Ex. 15, Chap. VI.

to take place in the cell 4 faradays of electricity would have to pass through the cell from the hydrogen to the oxygen electrodes, thus being raised through a potential of 1.227 volts. The work done on the counter-potential apparatus would, therefore, be $4 \times 96,500 \times 1.227$ joules, or 113,000 cals. (nearly). If, therefore, the change were conducted reversibly, this amount of available energy would be transferred from the cell to the counter-potential apparatus, instead of being degraded into thermal energy, and the heat received by the bath would be

$$137,000 - 113,000 = 24,000 \text{ cals.}$$

The heat absorbed during a *reversible* isothermal process, divided by the temperature, is equal to the entropy change, so the entropy of the bath has increased by $24,000/298 = 80.5$ units, and the entropy of the cell has decreased by the same amount. Taking everything concerned into account, the net entropy change is zero, as is always the case for reversible reactions which are only theoretical limits and not real processes at all. The separate parts of the system, however, suffer entropy changes as stated.

Returning to the case where the change takes place freely without any counter-potential apparatus, it is clear that the change undergone by the cell is just the same, and it therefore involves the same entropy decrease within the cell. The change in the bath is, however, different, since now 137,000 cals. are received by it. The entropy change is here $137,000/298 = 460$ entropy units (because this is the effect when 137,000 cals. are added reversibly to a bath at 25°C.), and so, if everything affected be again taken into account, the net increase in entropy of the free change is $460 - 80.5 = 379.5$ entropy units. This constitutes a measure of the tendency for the reaction to take place when it can do so freely at constant temperature and pressure.

The conclusions of this chapter may be summarised as follows:—

Entropy, denoted by the symbol S , is an intrinsic and extensive property of a system which cannot be measured in absolute terms (see, however, Chap. V.). Changes in entropy may, however, be measured by recourse to theoretical reversible processes whereby one obtains the equality,

$$\Delta S = \int_1^2 dQ_r/T = \int_2^1 -dQ_r/T,$$

where Q_r is the heat absorbed during the reversible change from state I. to state II. and $-Q_r$ is the heat evolved during the restoration from state II. to state I. Entropy has no simple physical significance, but is important because, as a result of the law of probability, any chemical or physical process which can occur spontaneously (i.e. can take place in an isolated system) must increase the entropy of the system as a whole. Reversible processes are imaginary because they leave the total entropy unchanged. Its greatest use is found in defining other, more convenient, terms (see Chap. III.), and on substituting it in equation (1), as applied to a reversible, and (for convenience) infinitesimal process, there is obtained the equation,

$$[dQ_r = T \cdot dS = dE + p \cdot dV + dW_r]_{\text{reversible}} \quad . \quad (1B)$$

which is required to deduce how these other terms vary with temperature and pressure. A more direct use of entropy is discussed in Chapter V.

CHAPTER III.

FREE ENERGY.

IN the first chapter it was shown how chemical affinity may be expressed in terms of the maximum work obtainable from a given process at constant temperature and pressure, while in the second it was expressed in terms of the total entropy change of everything affected. But the real cause of any spontaneous change under these conditions is the degradation of energy which results in the chemical system, the bath and atmosphere serving merely to define the change precisely, and so it is convenient to introduce a term which represents this intrinsic property of available energy. For this various notations have been employed by different authorities in spite of the fact that the whole ground was exhaustively covered in the original work of Willard Gibbs as far back as 1875. At the present day the influence of G. N. Lewis, who has done so much in applying the abstract formulæ of pure thermodynamics to the actual numerical measurement of the affinity of chemical reactions, is so great that it is most profitable to follow his system.

Lewis introduces two new terms. The first he calls the "Heat Content," and denotes by H . It is defined by the equation

$$H = E + pV \quad . \quad . \quad . \quad (2)$$

where E is the total energy content and V the volume of the chemical system, p being the pressure. It is at once obvious from the definition that H has the dimensions of energy, and is an intrinsic and extensive property of the system. Since the total energy of a system in absolute terms is always unknown, the same must be true for the heat content but, as we have to deal only with changes, it is always possible to assign some arbitrary value of H to the system in some one state under definite conditions and determine the value in any other state or

under other conditions relatively to this. Consequently, we are concerned primarily with the differential of the defining equation,

$$dH = p \cdot dV + V \cdot dp \quad . \quad . \quad . \quad (2A)$$

The relative heat content of a system is then obtained by integrating this expression between the limits set by the reference state and that for which the value is desired. For the particular case that the pressure is the same for both, the integral of equation (2A) is

$$(\Delta H = H - H^\circ = \Delta E + p \cdot \Delta V)_{p, \text{const.}} = Q_p \quad . \quad (2B)$$

where H° is the arbitrary value in the reference state and Q_p is the heat absorbed as measured when the change takes place in a constant pressure calorimeter without doing any extraneous work.

The second term Lewis calls the "Free Energy," and denotes by F . It differs slightly from the function called by the same name by many followers of Gibbs, but is identical with the latter's ζ commonly called the "thermodynamic potential." It is defined by the equation,

$$F = H - T \cdot S \quad . \quad . \quad . \quad (3)$$

where H and S are, respectively, the heat content and entropy of the chemical system (only) and T is the absolute temperature. Again, it follows from the definition that the free energy is an intrinsic and extensive property of the system which can be expressed numerically only in relative terms. By differentiation,

$$\begin{aligned} dF = dH - T \cdot dS - S \cdot dT &= dE + p \cdot dV + V \cdot dp \\ &\quad - S \cdot dT - T \cdot dS \end{aligned} \quad (3A)$$

This is connected with chemical affinity when applied to changes taking place at constant temperature and pressure, for then,

$$(dF = dE + p \cdot dV - T \cdot dS)_{p, T, \text{const.}} \quad . \quad . \quad (3B)$$

whilst from equation (1B), $(dE + p \cdot dV = T \cdot dS - dW_r)$,

$$\text{so} \quad (dW_r = -dF)_{p, T, \text{const.}} \quad . \quad . \quad . \quad (3C)$$

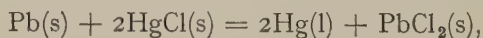
We are concerned with changes only, which corresponds to the integration of this equation between limits, thus not involving an integration constant, hence $(W_r = -\Delta F)_{p, T, \text{const.}}$, or, in words, *The maximum extraneous work obtainable from a reaction carried out at constant temperature and pressure is equal to the*

resulting decrease in free energy of the chemical system. It was shown in Chapter I. that the chemical affinity $(W_r)_{p, T, \text{const.}}$ of a change measures its tendency to take place, whether that tendency is allowed by chemical resistance to become manifest or not, and therefore, from equation (3c), the decrease in free energy as between the initial and final states of the chemical system measures the same thing. But we have now expressed it in terms of an intrinsic property, so that it is immaterial whether the actual change can be made to proceed reversibly at constant temperature and pressure or not, provided only that we can find by any means the difference between the free energies of the system in the two states at the same temperature and pressure. The most important corollary of this is that if two states of the same system can exist together in equilibrium they have the same free energy.* Thus, one gram-molecule of ice and one gram-molecule of liquid water are different states of the same system, but can exist together in equilibrium at atmospheric pressure and 0°C . Consequently, under these conditions, equal quantities of the same chemical substance, water, whether solid or liquid, have the same free energy.

The fact that F (and H) are extensive properties makes it possible to express the total value for the system as the sum of the values of the separate parts into which the system may conveniently be divided—these being, for the chemist, the gram-molecules of the various substances present. For example, in a system consisting of lead, mercury, lead chloride, and mercurous chloride, having a , b , c , and d gram-molecules of each, respectively, the total free energy

$$F = aF_{\text{Pb}} + bF_{\text{Hg}} + cF_{\text{PbCl}_2} + dF_{\text{HgCl}}$$

where F_{Pb} , F_{Hg} , etc., denote the molecular free energies of the substances indicated by the suffix. If the reaction,



takes place, one gram-molecule of lead chloride being formed, the free energy of the system will be changed to

$$F' = (a - 1)F_{\text{Pb}} + (b + 2)F_{\text{Hg}} + (c + 1)F_{\text{PbCl}_2} + (d - 2)F_{\text{HgCl}}.$$

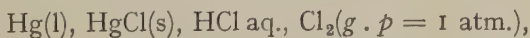
* As measured, of course, from the same reference state in each case.

Hence,

$$F' - F = \Delta F = 2F_{\text{Hg}} + F_{\text{PbCl}_2} - F_{\text{Pb}} - 2F_{\text{HgCl}},$$

and the negative value of this is the chemical affinity of the reaction. For any given change ΔF is fixed and may often be determined by experiment, but this alone does not enable us to fix the molecular free energies of the individual substances, which must themselves be relative to some arbitrarily-chosen value for some given state. A convenient system is, however, obtained if at any given temperature the value zero is assigned to the molecular free energies of all elements for some given state (crystalline, liquid, or gaseous) of each at some selected pressure, usually one atmosphere. The molecular free energy of compounds is then given at any temperature by the change in free energy consequent upon its formation from its elements in these selected reference states. If this be determined for a number of substances, the increase in free energy resulting from any reaction among them is obtained at once by adding together the molecular free energies of the resultants, each multiplied by the coefficient appearing in the equation expressing the reaction, and subtracting the corresponding sum of the molecular free energies of the reactants, also multiplied by the appropriate coefficients, just as in the above example. The chemical affinity of any reaction is thus reduced to an additive term, since it is given by the decrease of the free energy of the total system consequent upon the change. Thus, a complete table of the free energies of formation from their elements (in chosen states) of all substances for a given temperature and pressure would enable us to calculate the chemical affinities of all reactions under the same conditions.

Before the experimental measurement of numerical values for actual cases are considered, however, it is still necessary to study how free energy varies with temperature and pressure, for it so happens that what has been dealt with already is not sufficient for any case of the formation of a compound from its elements. It might appear that the free energy of formation of mercurous chloride could be obtained from the equilibrium electromotive force of the cell,



and this would be the case if the reaction of the cell were simply the formation of solid mercurous chloride from mercury and chlorine. In actual practice, however, disturbing effects are introduced at the chlorine electrode due to side reactions.

If a system be in equilibrium with the atmosphere, and the pressure of this be infinitesimally increased, there is, in general, a change of volume which occurs as a reversible process, no extraneous work is done, and the temperature may be kept constant by means of a bath. Applied to such a case, therefore, since dT and dW_r are both zero, equations (1B), (2A), and (3B) assume, respectively, the forms,

$$(dQ_r = T \cdot dS = dE + p \cdot dV)_{T, \text{const.}}$$

$$(dH = dE + p \cdot dV + V \cdot dp)_{T, \text{const.}}$$

and

$$(dF = dH - T \cdot dS)_{T, \text{const.}}$$

Combining these gives

$$(dF = V \cdot dp)_{T, \text{const.}} \quad . \quad . \quad . \quad (4)$$

This differential equation expresses quite rigidly the variation of free energy with pressure only, but in applying it to actual cases, integration is necessary, and this is only possible when we know the relation between V and p throughout the change. Usually approximations are employed for this latter relationship, and it is here, and here alone, that error may be introduced. Thus, with solids and liquids, it may be assumed without appreciable error that the volume is practically constant for moderate changes of pressure, when

$$\Delta F = V \cdot \Delta p \dots (4A).$$

To take mercury as an example, one gram-molecule occupies about 0.015 litre, so that a change in pressure of one atmosphere produces a change in free energy of 0.015 litre-atmosphere or 0.36 cal., an amount which is well within the experimental error of measurement of free energy changes. As a rule, the change of free energy with pressure of solids and liquids may be neglected.*

The larger molecular volume of gases, together with the great changes in the volume resulting from comparatively slight changes in pressure, calls for a different treatment. When they

* See, however, Ex. 13, Chap. VI.

may be regarded as perfect, $V = RT/p$ and $(dF = RT d \log_e p)_{T, \text{const.}}$, whence

$$(\Delta F = RT \log_e p_2/p_1)_{T, \text{const.}} \quad \cdot \quad \cdot \quad \cdot \quad (4B)$$

Since it is only the ratio of the final to the initial pressure which matters, very large changes in the free energy may be brought about by slight changes in the absolute pressure where this is low. It happens that in this case the *decrease* in free energy, $RT \log_e (p_1/p_2)$ is equal to the maximum work obtainable from the change, but this is a result of the particular equation of state for perfect gases for, by the rules of the calculus,

$$\int_1^2 V \cdot dp = p_2 V_2 - p_1 V_1 - \int_1^2 p \cdot dV$$

and for perfect gases at constant temperature,

$$p_2 V_2 = p_1 V_1, \text{ so } - \int_1^2 V \cdot dp = \int_1^2 p \cdot dV.$$

The student should be on his guard against assuming that the decrease of free energy, when pressure and temperature are not both kept constant, is in general equal to the maximum work obtainable from the change.

The great importance of our last equation lies in its application to gaseous mixtures. So far, we have dealt only with systems composed of an assemblage of pure substances, the exact conditions of each being determined by the state, pressure, and temperature. Where solution is possible, this is not enough, since the properties of the components will, in general, depend also upon the composition. A mixture of gases is really a solution, but in this case it is very nearly true to assume that each gas is uninfluenced by the others, and has the same properties as if it alone occupied the given volume. A component of a gaseous mixture under a total pressure of one atmosphere should therefore have the same molecular free energy as it has in the pure state at a pressure equal to its partial pressure in the mixture as calculated from Dalton's mixture law. The work of Masson and Dolley ⁴ shows that this assumption cannot be rigidly true, but for total pressures of the order of one atmosphere no appreciable error is introduced thereby, and it enables us to make some valuable deductions from gaseous equilibria.

This may be illustrated in reference to the concrete case of the formation of ammonia from its elements.

Consider an equilibrium mixture of hydrogen, nitrogen, and ammonia at some temperature T , the partial pressures being, respectively, p'_{H_2} , p'_{N_2} , and p'_{NH_3} , the strokes serving as a reminder that equilibrium conditions are postulated. The corresponding molecular free energies may similarly be denoted by F'_{H_2} etc. Let system A consist of a , b , and c gram-molecules of, respectively, hydrogen, nitrogen, and ammonia at the given partial pressures and temperature, while system B contains $(a - 3)$ gram-molecules of hydrogen, $(b - 1)$ gram-molecules of nitrogen, and $(c + 2)$ gram-molecules of ammonia, at the same partial pressures and temperature. A and B represent two chemically different states of the same system, the latter being obtained from the former by the reaction, $\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$, and since the partial pressures of the gases are the same, as is also the temperature, they could exist together side by side in equilibrium. Hence $F_B = F_A$, where F represents the total free energy of the system as a whole, the state being denoted by the suffix. But $F_A = aF'_{\text{H}_2} + bF'_{\text{N}_2} + cF'_{\text{NH}_3}$,

$$\text{and } F_B = (a - 3)F'_{\text{H}_2} + (b - 1)F'_{\text{N}_2} + (c + 2)F'_{\text{NH}_3},$$

whence, by addition, $2F'_{\text{NH}_3} - F'_{\text{N}_2} - 3F'_{\text{H}_2} = 0$.

That is, if the reaction be carried out under equilibrium conditions at constant temperature and pressure, there is no change in the free energy. But if $F^\circ_{\text{N}_2}$ represents the molecular free energy of nitrogen at the same temperature but atmospheric pressure, by (4B), $F'_{\text{N}_2} = F^\circ_{\text{N}_2} + RT \log_e (p'_{\text{N}_2}/I)$. Using a similar notation for the other gases,

$$2(F^\circ_{\text{NH}_3} + RT \log_e p'_{\text{NH}_3}) - (F^\circ_{\text{N}_2} + RT \log_e p'_{\text{N}_2}) - 3(F^\circ_{\text{H}_2} + RT \log_e p'_{\text{H}_2}) = 0,$$

$$\text{or } 2F^\circ_{\text{NH}_3} - F^\circ_{\text{N}_2} - 3F^\circ_{\text{H}_2} = -RT \log_e \frac{p'^2_{\text{NH}_3}}{p'_{\text{N}_2} \times p'^3_{\text{H}_2}}.$$

The left-hand side of this equation is definite and constant, being the difference in the intrinsic quantity, free energy, of a system in two chemically different states, (1) as one gram-molecule of nitrogen and three gram-molecules of hydrogen, each separately at one atmosphere pressure and temperature T , and (2) as two gram-molecules of ammonia at one atmosphere pres-

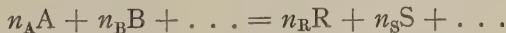
sure and the same temperature. It measures, therefore, the increase in free energy of the formation of ammonia from its elements, all being considered separately at atmospheric pressure and the same temperature. The right-hand side of the equation is also definite and constant, so long as the temperature is constant, and, therefore, the partial pressure quotient must be constant at constant temperature. This is, of course, the well-known equilibrium constant, usually denoted by K_p . The only restriction placed on the partial pressures in the course of the proof was that they should represent equilibrium values—it was not required that their sum should be one atmosphere, and it is only the quotient that must remain constant, the individual values may be varied according to circumstances.

In the present example Haber ⁵ has shown that a mixture containing the elements in the stoichiometrical proportions of ammonia at a total pressure of 100 atmospheres contained 10.4 per cent. ammonia when equilibrium was reached at 500° C. (773° K.). Thus the partial pressures in atmospheres are: 10.4 for the ammonia, 22.4 for the nitrogen, and 67.2 for the hydrogen, making $K_p = 1.59 \times 10^{-5}$. At a total pressure of 1 atmosphere, with the conditions otherwise unchanged, the equilibrium mixture contains 0.129 per cent. ammonia, which gives, of course, the same value of K_p . From this figure the increase of free energy resulting from the formation from its elements of two gram-molecules of ammonia gas at 500° C. and one atmosphere pressure is,

$$\Delta F = -RT \log_e K_p = 2.303RT \log_{10} K_p = -2.303 \times 1.987 \\ \times 773 \times (-4.7984) = +16,970 \text{ cal.}$$

and thus, under our conventions as to reference states, the gram-molecular free energy of ammonia as a gas at one atmosphere pressure and 500° C. is + 8485 cal.

The proof just considered can be made quite general, and it only remains to observe the conventions as to sign. For the reaction,



in the equilibrium constant the resultants appear in the numerator and the reactants in the denominator, thus,

$$K_p = \frac{p_R^{n_R} \times p_S^{n_S} \times \dots}{p_A^{n_A} \times p_B^{n_B} \times \dots}$$

and ΔF° refers to the increase of free energy resulting from the change expressed by the reaction reading from left to right, all substances being supposed to be separately at one atmosphere pressure. Then

$$\Delta F^\circ = -RT \log_e K_p \quad . \quad . \quad . \quad (5)$$

This provides a most valuable means of determining the free energy of any gas when the dissociation into its elements forms a measurable equilibrium. Incidentally, it may be observed that since ΔF° is always finite, all gaseous reactions must come in theory to a state of equilibrium with all the participants present to some extent, even though the partial pressures of some of them be extremely small. Pure liquids and solids, on the other hand, cannot vary their molecular free energies under constant conditions of temperature and pressure, and therefore will, in general, disappear completely as such, leaving only an imperceptible trace of themselves in the vapour state.

Since equilibria data have to be collected under favourable conditions of temperature, it is important to have a means of determining the variation of free energy with temperature. The temperature of a system may be raised infinitesimally at constant pressure as a reversible process, whence

$$dQ_r = T \cdot dS = dE + p \cdot dV$$

by equation (1B). But by (3A)

$$(dF = dE + p \cdot dV - T \cdot dS - S \cdot dT)_{p, \text{const.}}$$

so

$$(dF = -S \cdot dT)_{p, \text{const.}} \quad . \quad . \quad . \quad (6)$$

But, by equation (3),

$$-S = (F - H)/T.$$

Hence,

$$(dF/dT)_{p, \text{const.}} = (F - H)/T \quad . \quad . \quad (6A)$$

Two mathematical transpositions of equation (6A) are of frequent use, and may be given here. From the ordinary rules of the calculus,

$$\frac{d(F/T)}{dT} = \frac{T(dF/dT) - F(dT/dT)}{T^2},$$

and on substitution from (6A) we obtain,

$$\left(\frac{d(F/T)}{dT}\right)_{p, \text{const.}} = -\frac{H}{T^2} \quad . \quad . \quad . \quad (6B)$$

Again, from the laws of the calculus,

$$\frac{d(F/T)}{d(I/T)} = \frac{d(F/T)}{dT} \times \frac{dT}{d(I/T)} = \frac{d(F/T)}{dT} \times (-T^2).$$

On substitution from equation (6B),

$$(d(F/T)/d(I/T))_{p, \text{ const.}} = + H \quad . \quad . \quad (6c)$$

It should be remarked that equations such as (6B) cannot be directly employed for numerical calculation, since we have no means of measuring H in absolute terms. They can, however, be employed with comparative measurements when the comparison is of two states at the same temperature. Thus, if two different states of a given system at the same temperature, T be denoted by A and B respectively, the increase of free energy in changing from the first to the second is $\Delta F = F_B - F_A$. At the infinitesimally higher temperature $(T + dT)$ let the free energies be, respectively, F'_A and F'_B , and the increase of free energy in changing from the one state to the other at this higher temperature may be written $\Delta F + d(\Delta F) = F'_B - F'_A$. But, by equation (6), $F'_B = F_B - S_B dT$ and $F'_A = F_A - S_A dT$, whence, by subtraction, $d(\Delta F) = -\Delta S \cdot dT$. Consequently, all the equations derived from (6) are equally true applied to the increase of free energy and heat content resulting from a change of state without change of temperature, e.g.,

$$(d(\Delta F/T)/dT)_{p, \text{ const.}} = -\Delta H/T^2.$$

It is for this reason that the molecular free energy of all compounds is referred to their elements *at the same temperature*. On the other hand, in equation (4) and its derivatives, since V is known in absolute terms, the change in free energy of a system with change of pressure can be calculated directly. Nevertheless, if we wish to know how a change of state at constant pressure (and temperature) compares with the same change at a different (but constant) pressure, it may be shown in a similar manner that $d(\Delta F) = \Delta V \cdot dT$.

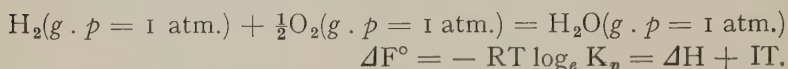
The most generally useful of all these equations is (6B) applied to chemical reactions, and therefore in the form

$$d(\Delta F/T) = (-\Delta H/T^2)dT,$$

which is rigidly true, since it depends only upon the two laws of thermodynamics. In application, however, it is required in the

integral form, and for this the relation between ΔH and T must be known. Here some error may be, and usually is, introduced, though it may be reduced to very small dimensions at the expense of complicating our formulæ. In many cases it is sufficient to treat ΔH as a constant when we have the very simple integral, $(\Delta F/T) = (\Delta H/T) + I$, where I is a constant of integration to be determined by experiment. Hence, $\Delta F = \Delta H + IT$.

A good example where this approximation is justified is offered by the formation of water vapour from its elements at high temperatures according to the equation,



The heat evolved on the formation of one gram-molecule of liquid water from its elements at 0°C. is about 68,500 cal. according to Lewis,⁶ and we will assume that this is the same at 100°C. The heat absorbed when one gram-molecule of liquid water is vaporised at 100°C. is 9730 cal. according to Smith,⁷ and this amount of heat would be evolved when the vapour condensed at this temperature. Accordingly, if water vapour is formed from its elements at 100°C. without condensation, the heat evolved should be 58,770 cal. per gram-molecule, making ΔH (heat absorbed) = - 58,770 cal., which we will assume to be constant and independent of temperature. The equilibrium constant, $K_p = p_{\text{H}_2\text{O}}/p_{\text{H}_2} \times p_{\text{O}_2}^{\frac{1}{2}}$, has been determined from vapour pressure measurements at high temperature. Taking Langmuir's⁸ figures at 1433°K. , water vapour is 0.0103 per cent. dissociated, whence $K_p = 1/(0.000103 \times 0.000052^{\frac{1}{2}}) = 1.35 \times 10^6$. Thus,

$$\Delta F^\circ_{1433} = 2.303RT \log_{10} (1.35 \times 10^6) = -40,230 \text{ cal.}$$

But
$$\Delta F^\circ_{1433} = -58,770 + 1433 \times I,$$

therefore, $I = +12.94$ and the general equation becomes,

$$\Delta F^\circ = -58,770 + 12.94 T.$$

If ΔF° be worked out from this equation and compared with the values obtained from experimental determinations of the equilibrium constant, as is shown in the table below, no appreciable disparity exists, although the assumption that ΔH is

constant is not strictly valid. The figures are taken from the same paper by Langmuir :—

T.	ΔF° calc.	Per Cent. diss.	K_p (exp.).	$-RT \log_e K.$
1325	— 41,620	0.00325	7.65×10^8	— 41,670
1354	— 41,240	0.0049	4.13×10^8	— 41,010
1393	— 40,740	0.0069	2.47×10^8	— 40,670
[1433]	— 40,230	0.0103	1.35×10^8	— 40,230]
1455	— 39,940	0.0142	8.35×10^7	— 39,450
1474	— 39,690	0.0141	8.45×10^7	— 39,990
1531	— 38,960	0.0255	3.47×10^7	— 38,830
1550	— 38,710	0.0287	2.91×10^7	— 38,760

On the other hand, many cases occur where this approximation leads to considerable error. An illustration is afforded by the vaporisation of a liquid, say water, according to the equation $H_2O(l) = H_2O(g \cdot p = 1 \text{ atm.})$, which we will denote by (a). It may be represented as the sum of two equations,



where p is the vapour pressure of the liquid at the temperature in question, and (c) $H_2O(g \cdot p \text{ atm.}) = H_2O(g \cdot p = 1 \text{ atm.})$. Reaction (a) could be attained by reactions (b) and (c) in succession, so $\Delta F_a = \Delta F_b + \Delta F_c$. Of these, $\Delta F_b = 0$ since it is the free energy change of a reaction taking place under equilibrium conditions, and $\Delta F_c = RT \log_e (1/p) = -RT \log_e p$. Hence,

$$\Delta F_a = -RT \log_e p.$$

But also, $\Delta F_a = \Delta H_a + IT$. We have seen that at 100°C . $\Delta H_a = 9730 \text{ cal.}$, while at this temperature $p = 1$, so $\Delta F_{373} = 0$.

Therefore $I = -\frac{9730}{373} = -26.09$. Combining the equations and substituting in the numerical values,

$$-RT \log_e p = 9730 - 26.09 \times T,$$

$$\begin{aligned} \text{or } \log_{10} p &= (26.09/2.303 \times 1.9879) - (9730/2.303 \times 1.9879 \times T) \\ &= 5.70 - (2125/T). \end{aligned}$$

The following table shows that the values of p , the vapour pressure of water, obtained from this equation differ decidedly from those obtained experimentally, the error being due to the assumption that the heat of volatilisation is constant.

t° C.	T° K.	log ₁₀ p.	p _{calc.}	p _{expl.}
0	273	— 2.094	0.0080	0.00605
50	323	— 0.821	0.151	0.121
[100	373	0.0000	1.000	1.000]
160	433	0.793	6.2	6.1
200	473	1.206	16.1	15.4

It is therefore desirable to study further how ΔH varies with temperature in order to be able to integrate $(-\Delta H/T^2)dT$ more accurately. The exact relation was worked out by Kirschhoff along the following lines: Consider a system in state A at temperature T and pressure p. Let some chemical reaction take place at constant temperature and pressure bringing the system into state B with an increase of heat content ΔH , which may be measured calorimetrically. Then warm the system at constant pressure up to $T + dT$, during which operation the heat content is increased by $C_B \cdot dT$, where C_B is the thermal capacity of the system in state B. Thus,

$$H_{B(T+dT)} - H_{A_T} = \Delta H + C_B \cdot dT.$$

The left-hand side of the equation indicates the excess heat content of the system in state B at temperature $T + dT$ over that in state A at temperature T. Since heat content is an intrinsic property, this is quite definite and independent of the path by which the change was carried out. Again, we might start with the system in state A at temperature T and warm it up to $T + dT$, when the increase in the heat content is $C_A \cdot dT$, where C_A is the thermal capacity of the system in state A. The change from state A to state B can now take place at constant temperature and pressure, with an increase of heat content of

$$\Delta H + d(\Delta H).$$

Then,

$$H_{B(T+dT)} - H_{A_T} = C_A \cdot dT + \Delta H + d(\Delta H).$$

Hence,

$$d(\Delta H) = (C_B - C_A)dT = \Delta C \cdot dT \quad . \quad . \quad (7)$$

But ΔC is itself a function of temperature which requires to be known before integration is possible. The full discussion of this is deferred until later, for the present it is sufficient to state that the thermal capacity of most substances can be represented

from normal room temperatures upward by formulæ of the power type, $C_p = a' + b'T + c'T^2 + \dots$, but it cannot be too strongly emphasised that such formulæ are purely empirical and *valid only for that region of temperature for which they are designed*. Extrapolation towards either higher or lower temperature invariably leads to error. With this restriction we may represent $\Delta C_p = a + b \cdot T + c \cdot T^2 + \dots$ where a is the sum of the a' terms of the resultants less those of the reactants, and so on. Consequently, from equation (7),

$$\Delta H_T = \Delta H_0 + a \cdot T + \frac{1}{2}b \cdot T^2 + \frac{1}{3}cT^3 + \dots \quad (7A)$$

where ΔH_0 is an empirical integration constant, and cannot be regarded as the actual heat of reaction at the absolute zero of temperature since the fundamental formulæ (of the heat capacities) are not valid in that region.

On substituting this into equation (6B) (as applied to a chemical reaction)

$$d(\Delta F/T) = - [(\Delta H_0/T^2) + (a/T) + \frac{1}{2}b + \frac{1}{3}c \cdot T + \dots] dT,$$

and on integrating

$$\Delta F/T = + (\Delta H_0/T) - a \cdot \log_e T - \frac{1}{2}bT - \frac{1}{6}c \cdot T^2 - \dots + I,$$

where I is a constant of integration to be determined by experiment. Thus,

$$\Delta F = \Delta H_0 - a \cdot T \cdot \log_e T - \frac{1}{2}b \cdot T^2 - \frac{1}{6}c \cdot T^3 - \dots + IT \quad (7B)$$

Such an equation is called a "general free energy equation." The minimum data required to give it numerical form in any given case are (1) The heat capacity formulæ of all the substances concerned over the range of temperature for which it may be used; (2) One measurement of the heat of reaction at some temperature within that range (to obtain ΔH_0); and (3) One measurement of ΔF at some temperature within the range of validity of the heat capacity formulæ (from which to obtain I).

Since $\Delta F^\circ = -RT \log_e K_p$ is only a special case of ΔF , an equation of this type serves to express the variation of the equilibrium constant, usually in the transposed form

$$\log K_p = - \frac{\Delta H_0}{2 \cdot 303RT} + \frac{a \cdot \log_{10} T}{R} + \frac{\frac{1}{2}b \cdot T}{2 \cdot 303R} + \frac{\frac{1}{6}c \cdot T^2}{2 \cdot 303R} + \dots - \frac{I}{2 \cdot 303R}.$$

It has to be admitted, however, that the heat capacity data for gases have been chosen far more to suit well-determined equilibria data than from experimental measurement.

So far as has been discussed, there are only two distinct experimental methods of measuring free energy changes, and both involve the determination of an equilibrium.

The first is applicable to such reactions as are capable of forming the working process of a reversible galvanic cell. In this case the equilibrium counter-potential, E , which just arrests the change without reversing it, is measured, and the maximum work available from the process is E volt faradays per gram equivalent, or $23,060 \cdot E$ cals. per gram equivalent. If the reaction involves n gram equivalents, the maximum work available, equal to the chemical affinity and, by equation (3c) to $-\Delta F$, is $23,060 \cdot n \cdot E$ cals. This is illustrated in the case of the reaction



on page 11. Not all galvanic cells are reversible. For example, if oxygen and hydrogen electrodes, dipping into dilute sulphuric acid, are connected, they will cause a current to flow through the connecting wire and the formation of water will take place in the cell. Moreover, if they be connected to a sufficiently great counter-potential, the current will pass through the cell in the reverse direction, electrolysing the solution and liberating oxygen and hydrogen. But the least counter-potential necessary to prevent all signs of current flowing is considerably less than the least value necessary to produce perceptible electrolysis. Consequently, no sharp determination of an equilibrium potential is possible. Such a cell is said to be irreversible (quantitatively), the effect being due to the slowness with which the oxygen electrode comes into equilibrium with the oxygen above when the small, but finite, change necessary to observe electrolysis is imposed upon it. Consequently, the oxygen electrode is not in equilibrium with the gas under the conditions of experiment. All electrodes must be irreversible to some extent, so the difficulty is one of degree rather than of kind.

It should also be observed that, even when the degree of reversibility is very high, as is the case with an electrode of silver dipping into silver nitrate solution, the observed electromotive

force varies slightly with the condition of the silver, its previous thermal treatment and the like. This shows that the molecular free energy is not entirely defined by pressure and temperature alone—even the size of the particles in a granulated mass is of some importance—but the effect of other factors is usually small (except, perhaps, in the case of colloids), and may be neglected in an elementary exposition.

The second method is applicable to all cases of gaseous equilibrium. The partial pressures of the gases under equilibrium conditions are determined from the composition, total pressure, and the gas laws and, from them, the constant K_p is calculated. Then, ΔF° , representing the free energy change resulting from the conversion of the reactants (each separately at one atmosphere pressure) into the resultants (also each separately at one atmosphere) is given by equation (5) as equal to $-RT \log_e K_p$. This is illustrated in the case of the free energy of formation of ammonia on page 38.

This method applies equally well to heterogeneous reactions because, if sufficient solids * be present, the reaction does not proceed to completion, but only so far that the molecular free energy of the gases concerned have altered with their partial pressures until $\Delta F = 0$. It is sometimes helpful to think of the reaction taking part in the gaseous phase, the vapours of the solids being kept at constant partial pressure (and, therefore, at constant molecular free energy) by the presence of the solid material. Thus it is only those substances which are present solely as gases which appear in K_p . The dissociation of calcium carbonate furnishes an example. The reaction is



and at 740°C . the equilibrium (partial) pressure of the carbon dioxide is 255 mm. = 0.3355 atm.

Thus,

$$F^\circ_{\text{CaO}(\text{s})} + F_{\text{CO}_2(\text{g}, p = 0.3355 \text{ atm.})} - F^\circ_{\text{CaCO}_3(\text{s})} = 0 = \Delta F.$$

* The pressure of liquids, in general, gives rise to solutions which are considered in the next chapter. If, however, the liquids remain sensibly pure, as is usually the case with mercury, the treatment is the same as for solids.

But

$$\begin{aligned}
 \Delta F^\circ &= F^\circ_{\text{CaO(s)}} + F^\circ_{\text{CO}_2(g, p=1 \text{ atm.})} - F^\circ_{\text{CaCO}_3(s)} \\
 &= \Delta F + F^\circ_{\text{CO}_2(g, p=1 \text{ atm.})} - F^\circ_{\text{CO}_2(g, p=0.3355 \text{ atm.})} \\
 &= RT \log_e (1/0.3355) = -RT \log_e K_p \\
 &= 2.303 \times 1.987 \times 1013 (-0.4743) \\
 &= +2200 \text{ cal.}
 \end{aligned}$$

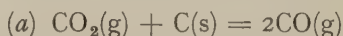
The chemical affinity ($= -\Delta F^\circ$) for the dissociation of calcium carbonate at 740°C. into carbon dioxide at atmospheric pressure and lime is therefore negative, -2200 cal. , i.e. carbon dioxide at atmospheric pressure and lime have, at 740°C. , an intrinsic tendency ($+2200 \text{ cal.}$) to combine.

A similar treatment is accorded to cases of equilibrium in solution, where it was at first proposed to employ concentrations in the calculation of an analogous constant to K_p . This, however, requires modification, as will be seen in the next chapter.

Measurements of equilibrium are usually possible only within a limited range of temperature, and consequently it is only within this range that free energy changes can be directly determined. Values at other temperatures may, however, be obtained by means of equation (6) (and its derivatives), when the necessary thermal data are available.

A third experimental method of determining free energy changes, not involving the measurement of an equilibrium, will be discussed in Chapter V.

Lastly, free energy changes are additive, and may be determined indirectly. For example, the reaction



gives rise to a measurable equilibrium from which, at 25°C. , $\Delta F^\circ_a = +29,240 \text{ cal.}$ has been calculated.³ Similarly, the reaction $(b) \text{CO}_2(g) = \text{CO(g)} + \frac{1}{2}\text{O}_2(g)$ gives rise to a measurable equilibrium, from which $\Delta F^\circ_b = +61,750 \text{ cal.}$ has been calculated.³ But the reaction $(c) \text{C(s)} + \frac{1}{2}\text{O}_2(g) = \text{CO(g)}$ does not give rise to a measurable equilibrium, so that the resulting free energy change, ΔF°_c , cannot be measured directly. Equation (c) is, however, obtained by subtracting (b) from (a), i.e. reaction (c) could be obtained by reaction (a), followed by reaction (b) reversed, consequently

$$\Delta F^\circ_c = \Delta F^\circ_a - \Delta F^\circ_b = -32,510 \text{ cal. at } 25^\circ \text{C.}$$

This treatment is entirely the same as that employed for the indirect determination of heats of reaction.

CHAPTER IV.

SOLUTIONS.

PARTIAL MOLECULAR QUANTITIES.—The properties of pure substances are completely defined for any given state, temperature and pressure,* and even for mixtures of perfect gases, since the various components have no effect on each other, the properties of each are defined by the temperature and partial pressure. For solutions in general, however, where the different molecular species interpenetrate and affect each other, the extensive properties such as the volume, heat content, and free energy, are not strictly additive, although often very nearly so. To take rather an extreme example of departure from the additive law, Hill and Sirkar ⁹ have shown that at 0° C. 50 grams of water and 50 grams of hydrogen fluoride (which separately occupy, respectively, 50.01 and 49.98 c.c.) when mixed have a volume of only 82.80 c.c. instead of the 99.99 c.c. to be expected by addition. The problem of assigning the responsibility, so to speak, for the volume between the two components therefore arises.

A solution of the problem would be offered if it were possible to add the components separately without altering the concentration, a process which is nearly realised by adding a small quantity of either component to a very large volume of the mixture. It may be calculated from the data of Hill and Sirkar (by a method to be given immediately) that if this were done, each gram of water, added to and mixed with a very large volume of 50 per cent. hydrofluoric acid, would increase the volume by 0.9540 c.c., so that 18 grams (one gram-molecule) would increase the volume by 17.172 c.c. This, then, is the effective volume of one gram-molecule of water in acid of this strength, called (by analogy with the

* This is not quite rigidly true (cf. the varying e.m.f. of metals according to their method of preparation), but is sufficiently nearly so for our purpose.

partial pressures of gases) the "partial molecular volume" of water in 50 per cent. hydrofluoric acid. In practice, the volume of acid with which one started would have to be very large indeed, so that the concentration should not be appreciably altered by the addition of the water, for the partial molecular volume varies with the concentration. Thus, with 75 per cent. acid, the partial molecular volume of the water is 14.562 c.c.

The practical difficulties of such a method are considerable, and it is simpler to employ the calculus. Let V be the volume containing A gram-molecules of hydrogen fluoride and X gram-molecules of water, where A is a constant and X is variable. If V be determined for a series of values of X , we may express the relation between them in the form of an equation or a curve, and dV/dX at any point expresses accurately the increase of volume that would result if one gram-molecule of water were added without increasing the concentration, a result which could be achieved in practice only by using an infinite quantity of acid in the beginning.

A useful method of treatment of such binary solutions, due to Roozeboom,¹⁰ may be illustrated. Let V be the volume of solution containing n_1 grams of water and n_2 grams of hydrogen fluoride. Then the specific volume, $v = V/(n_1 + n_2)$. If n_1 alone be varied

$$\left[dv = \frac{(n_1 + n_2) \cdot dV - V \cdot dn_1}{(n_1 + n_2)^2} \right]_{n_2 \text{ const.}}$$

Let x be the fraction of the total weight due to the hydrogen fluoride, then $x = n_2/(n_1 + n_2)$,

whence
$$\left[dx = -\frac{n_2 \cdot dn_1}{(n_1 + n_2)^2} \right]_{n_2 \text{ const.}}$$

Plotting the specific volume against the fraction x , as in Fig. 2, the tangent to the curve at any point gives, by division of the two equations above,

$$\frac{dv}{dx} = \frac{-(n_1 + n_2) \cdot dV}{n_2 \cdot dn_1} + \frac{V}{n_2}$$

or
$$-\frac{n_2}{n_1 + n_2} \cdot \frac{dv}{dx} = \frac{dV}{dn_1} - \frac{V}{n_1 + n_2},$$

but dV/dn_1 is the partial specific volume of the water (corresponding to dV/dX above), which may be denoted by $\bar{v}_1$, and $V/(n_1 + n_2) = v$, the specific volume, hence

$$\bar{v}_1 = v - \frac{n_2}{n_1 + n_2} \cdot \frac{dv}{dx}.$$

$V =$ Specific Volume of Solution.

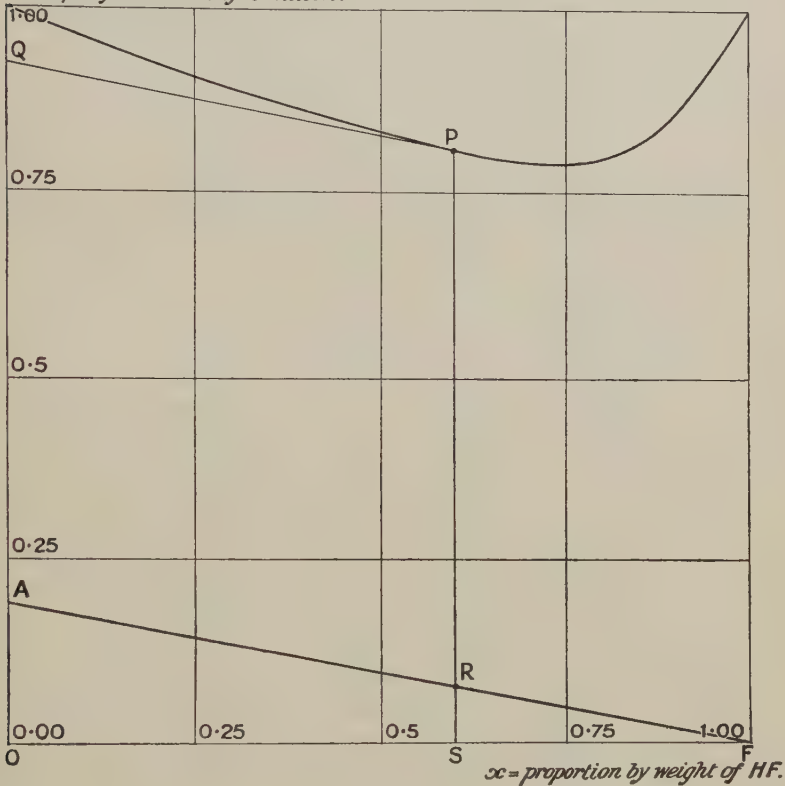


FIG. 2.

Comparing this equation with Fig. 2, in which $\overline{QP}$ is drawn tangent to the curve at P and $\overline{AF}$ is parallel to $\overline{QP}$ through the intercept of the axes at F, it will readily be seen that

$$\overline{OA} = - (dv/dx),$$

$$\overline{SP} = v, \text{ and } \overline{SR} = \frac{n_1}{n_1 + n_2} \cdot \overline{OA} = \frac{-n_1}{n_1 + n_2} \cdot \frac{dv}{dx}.$$

The intercept on the water axis, $\overline{PQ}$, which the tangent, $\overline{QP}$, to the curve makes is seen to be given by the equation

$$\begin{aligned}\overline{OQ} &= \overline{OA} + \overline{PR} = \overline{OA} - \overline{SR} + \overline{SP} \\ &= -\frac{dv}{dx} + \frac{n_1}{n_1 + n_2} \cdot \frac{dv}{dx} + v = -\frac{n_2}{n_1 + n_2} \cdot \frac{dv}{dx} + v.\end{aligned}$$

Hence, $\overline{OQ} = \bar{v}_1$. Similarly, the intercept of the tangent on the hydrogen fluoride axis gives $\bar{v}_2$, the specific partial volume of the hydrogen fluoride in acid of the strength indicated by the point S. The data from which the curve was drawn are given below.*

DENSITY AND SPECIFIC VOLUME OF HYDROFLUORIC ACID AT 0° C.

Grams.		d°_4	v
H ₂ O.	HF.		
0.0000	1.0000	1.0005	0.9995
0.0498	0.9502	1.082	0.924
0.0897	0.9103	1.164	0.859
0.1125	0.8875	1.208	0.828
0.1494	0.8506	1.232	0.813
0.2307	0.7693	1.262	0.792
0.2620	0.7380	1.261	0.793
0.3683	0.6317	1.247	0.802
0.4330	0.5670	1.230	0.813
0.5465	0.4535	1.172	0.853
0.7155	0.2845	1.110	0.901
0.7860	0.2140	1.085	0.922
0.8790	0.1210	1.047	0.955
0.9390	0.0610	1.028	0.973
1.0000	0.0000	0.9998	1.0002

The molecular partial volume, $\bar{V}_1$, is obtained by multiplying the specific value by the assumed molecular weight. In all these calculations, the so-called molecular weight is merely a convenient unit of quantity, like the gram or the ounce, and it is only when we have to do with kinetic laws, such as the perfect gas law, that it makes any difference what value is chosen. In general, we do not know the molecular weight in the liquid state, and assume it to be the same as that shown by the sub-

* Once the proof has been established, $\overline{AF}$ is not required, and the scale of the axis V is chosen as large as possible, omitting the lower values (below 0.75 say) which are not required.

stance in the state of vapour. Solutions are often dealt with formally without respect to the different species of molecules present. Thus, if a given solution of hydrofluoric acid contains n_1 gram-molecules of water and n_2 gram-molecules of hydrogen fluoride in a volume V , the molecular volume of the solution as a whole is said to be $V/(n_1 + n_2)$ by analogy with the specific volume. Doubtless, behind this assumption there is the idea that Avogadro's number of individual molecules is present in this volume, although they are not all of one kind, but the formal treatment is the same even when it is quite certain that some chemical reaction such as solvation or dissociation makes this simple conception impossible. An important method of expressing concentration may also be defined here. If a solution contains $n_A, n_B, \dots n_X$ gram-molecules, respectively, of substances A, B, $\dots$ and X, then $n_A/(n_A + n_B + \dots + n_X)$ is called the "molar fraction" of A, and similarly for the other substances. This, too, is entirely formal, and takes no cognisance of possible changes of molecular weight through chemical reaction.

The definition that has been given of "partial molecular volume" may be extended to any other extensive property of a system, such as the heat content or free energy. There is no essential difference between these "partial" properties and the heat content and free energy of pure substances, so that all the equations developed in the previous chapters apply equally to both. Indeed, no substance has ever been prepared in a state of complete purity, so that there can exist no line of demarcation between the two. Thus $(d\bar{F}_1 = \bar{V}_1 \cdot dp)_{T, x, \text{const.}}$ is merely the adapted form of equation (4), and denotes that the change of partial molecular free energy of substance 1 is, for an infinitesimal change, equal to the product of its partial molecular volume into the change of pressure, when the temperature and composition are kept constant. The symbol x will be employed to denote composition (or concentration) whenever it is not required to specify more exactly the way in which composition is to be expressed.

An extremely important relationship between the partial molecular quantities of the components in a solution will now be demonstrated for volume, this being the easiest property to study, but the same treatment may be applied to any of the other properties which are similarly intrinsic and extensive.

Suppose that, to a quantity of solution containing water and hydrogen fluoride in the proportions of n_1 gram-molecules of the former to n_2 gram-molecules of the latter, n_1 gram-molecules of water and n_2 gram-molecules of hydrogen fluoride are simultaneously added in these proportions (e.g. by continuous addition from burettes). The increase in volume, V , is the volume of solution which contains the amounts of the components added. But, since the composition never varied, each gram-molecule of water added increased the volume by $\bar{V}_1$, its partial molecular volume in acid of this concentration, and each gram-molecule of hydrogen fluoride similarly increases the volume by $\bar{V}_2$. Consequently, $V = n_1 \cdot \bar{V}_1 + n_2 \cdot \bar{V}_2$, and on differentiating,

$$dV = n_1 \cdot d\bar{V}_1 + \bar{V}_1 \cdot dn_1 + n_2 \cdot d\bar{V}_2 + \bar{V}_2 \cdot dn_2.$$

But the properties which we have called "intrinsic" are those whose values are, in the language of mathematics, "complete differentials," and, therefore, by partial differentiation,*

$$dV = \left(\frac{\delta V}{\delta n_1} \right) \cdot dn_1 + \left(\frac{\delta V}{\delta n_2} \right) \cdot dn_2 = \bar{V}_1 \cdot dn_1 + \bar{V}_2 \cdot dn_2.$$

By subtraction from the above equation,

$$n_1 \cdot d\bar{V}_1 + n_2 \cdot d\bar{V}_2 = 0 \quad . \quad . \quad . \quad (8)$$

This proof may be extended to any number of components, and applied to any intrinsic and extensive property, so that, for example,

$$n_1 \cdot d\bar{F}_1 + n_2 \cdot d\bar{F}_2 + n_3 \cdot d\bar{F}_3 + \dots = 0 \quad . \quad . \quad . \quad (8A)$$

ACTIVITY.—Since chemical reactions are far more often carried out in solution than with an assemblage of pure substances, the variation of partial molecular free energy with the proportions of the components is of prime importance to the study of chemical affinity. This is most readily determined where the component under consideration exerts a measurable vapour pressure, and the vapour above the solution may be treated as a perfect gas (or mixture of perfect gases). Consider two solutions, X and X', at the same pressure and temperature, and differing only in the proportions of the components. Let

* For a clear account of the mathematics of partial differentiation see (for example) *Higher Mathematics for Students of Chemistry and Physics*, by Mellor, 1916, p. 68 (Longmans, Green & Co.).

the vapour pressure of one component above these be p and p' , respectively. The substance in the vapour state at these pressures is, therefore, in equilibrium with the same substance in the solutions, and has the same molecular free energy in each case in the two states. Consequently, the difference in its (partial) molecular free energies in the two solutions is the same as that in the two vapours, or $\bar{F}' - \bar{F} = RT \log_e (p'/p)$.

In many cases the vapour pressure is proportional to the concentration (Henry's law), in which case the ratio of the concentrations instead of the vapour pressures could be employed. But this law is not always true, and it is therefore convenient to invent a new term which, by definition, can be substituted in the above equation in place of the vapour pressures and gives, rigidly, the difference in the free energies, while at the same time it may be related to the concentration in such a manner as to be equal to it (the concentration) when Henry's law is obeyed: when it is not, the relation between this new term and the concentration must be determined by experiment.

We may use the notation of G. N. Lewis and call this new term the "activity," and denote it by " a ." Its purpose is purely comparative (at constant temperature), that is, it is only the ratio of activities which matter, absolute values being obtained by choosing some one state for each component and assigning an arbitrary value of activity to it according to convenience. The essential definition may, therefore, be put in the form of a differential equation at constant temperature,

$$[dF(\text{or } d\bar{F}) = RT d \log_e a]_{T, \text{const.}} \quad . \quad . \quad (9)$$

Then the definite integral, corresponding to a change between specified states, is given as above by

$$[\Delta F (\text{or } \Delta \bar{F}) = F' - F = RT \log_e (a'/a)]_{T, \text{const.}} \quad . \quad (9A)$$

Although there is nothing in this definition to prevent it, activity is not employed in connection with chemical changes, but only with the changes in molecular free energy of substances with concentration, pressure, or, more rarely, with changes of state.

The application of this term lies in the comparison of the chemical affinity between substances, all of which are in those states to which, by our arbitrary choice, unit activity is assigned

with that when the substances are in other states. Consider the general equation,

$$n_A A(a=1) + n_B B(a=1) + \dots = n_R R(a=1) + n_S S(a=1) + \dots$$

and denote the free energy change of this reaction by ΔF° , then compare it with

$$n_A A(a=a_A) + n_B B(a=a_B) + \dots = n_R R(a=a_R) + n_S S(a=a_S) + \dots$$

for which the free energy change may be denoted by ΔF .

The first of these reactions may be carried out in stages:—

- (1) Each of the reactants may be brought from unit activity to that recorded in the second reaction. This, for the substance A involves a free energy change,

$$\Delta F_A = n_A \cdot RT \log_e (a_A/1),$$

and similarly for the others.

- (2) The second reaction may then be supposed to take place, leaving the resultants at the activities indicated in the second equation.

- (3) Each of the resultants may now be brought to unit activity. For the substance S this involves a free energy change of

$$\Delta F_S = n_S \cdot RT \log_e (1/a_S).$$

Hence,

$$\Delta F^\circ = \Delta F_A + \Delta F_B + \dots + \Delta F + \Delta F_R + \Delta F_S + \dots$$

$$\text{or} \quad \Delta F^\circ = \Delta F - RT \log_e \frac{a_R^{n_R} \times a_S^{n_S} \times \dots}{a_A^{n_A} \times a_B^{n_B} \times \dots} \quad (10)$$

An important deduction from this is that if a_A , a_R , etc., happen to be such that equilibrium exists, $\Delta F = 0$. But ΔF° is a constant, being simply the difference of free energy between two defined states of the system at constant temperature. Consequently, the quotient following the logarithm must be a constant at constant temperature for all possible states of equilibrium, it is therefore the equilibrium constant, denoted by K , and

$$\Delta F^\circ = -RT \log_e K \quad (10A)$$

The proof is identical with that employed in deriving K_p , which was a particular case, for with perfect gases the partial pressure

is proportional to the activity. But if the gases were not perfect this proportionality would not exist and, since K must be constant by the definition of activity, K_p would not be unless by some extraordinary compensation of errors. The same is true for the equilibrium constant of solutions. Where activities are proportional to concentrations the ordinary equilibrium constant in which concentrations are employed must hold good, but when activity is not proportional to concentration this cannot be true. While the simple relationship that the vapour pressure is proportional to the concentration (suitably expressed) holds good over a wide range of concentration in a few cases, and approximates very closely to the facts in dilute solution only in a great many more, there are many cases in which wide divergence from this law is found, even in very dilute solution, so the proportionality between vapour pressure (where the vapour is a perfect gas) and activity should be kept in view rather than the relation between activity and concentration. It is still better, though less tangible, to regard it solely as a means of expressing conveniently the relation between molecular free energy and condition at constant temperature.

Vapour pressures, however, are comparatively rarely susceptible of accurate measurement, especially in dilute solution where the bulk of the progress in theoretical chemistry has been made, and a more important practical method of studying the variation of activity with concentration is offered by the measurement of the freezing-point of solutions sufficiently dilute for the pure solvent to separate in the solid phase. Then, for that particular temperature (the freezing-point), the pure solid solvent is in equilibrium with the solvent in the solution and

$$[F_s - F_1^\circ = \bar{F}_1 - F_1^\circ]_{\text{freezing-point}},$$

where F_s , F_1° , and $\bar{F}_1$ are, respectively, the molecular free energies of the pure solid and liquid solvent and the partial molecular free energy of the solvent in the solution. But, by equation (6B), $d\left(\frac{F_s - F_1^\circ}{T}\right) = -\frac{\Delta H}{T^2} \cdot dT$, where ΔH is the heat absorbed when one gram-molecule of pure solvent solidifies, so $-\Delta H = L$, the molecular latent heat of fusion of the pure solvent. It is more convenient to measure the depression of the freezing-point, θ , that is the number of degrees below the freezing-point of the

pure solvent, θ , at which the solution is in equilibrium with the solid solvent, than the absolute value, so the equation is adapted by substituting $\theta - \mathfrak{J} = T$, whence $-d\mathfrak{J} = dT$. Moreover, L is itself a function of temperature. Since it is the heat absorbed when one gram-molecule of solid solvent melts, by equation (7), $dL = (C_1^\circ - C_s) \cdot dT$, where C_1° and C_s are, respectively, the molecular heat capacities of the pure solvent in the liquid and solid states. Since the former is always greater than the latter, L increases with T and diminishes with $\mathfrak{J}$. Finally, we write $F_s - F_1^\circ = RT \log_e a_s$, and $\bar{F}_1 - F_1^\circ = RT \log_e a_1$, where a_s and a_1 are, respectively, the activities of the solid solvent, and the solvent in the solution when the activity of the pure liquid solvent at the same temperature is arbitrarily set equal to unity, and note that these are equal at the freezing-point of the solution, giving

$$\log_e a_{s_{\theta-\mathfrak{J}}} = \log_e a_{1_{\theta-\mathfrak{J}}} = \int_0^{\mathfrak{J}} \left(\frac{-L}{R(\theta - \mathfrak{J})^2} \right) d\mathfrak{J} \quad . \quad (II)$$

The integration of equation (II) is clumsy, though it may always be effected, giving an equation of the power type. For dilute solutions where $\mathfrak{J}$ is small no great error is introduced by using the approximation

$$\log_e a_{1_{\theta-\mathfrak{J}}} = \int_0^{\mathfrak{J}} (-L_\theta/R\theta^2) \cdot d\mathfrak{J} \quad . \quad . \quad (IIA)$$

This would not be far wrong for values of $\mathfrak{J}$ not greater than one or two degrees even when the two terms affected, L and $(\theta - \mathfrak{J})$ are considered separately, while also compensation is introduced by the fact that, as $\mathfrak{J}$ increases, L becomes less than L_θ and $(\theta - \mathfrak{J})$ becomes less than θ , so that both numerator and denominator are decreasing together, thereby keeping their ratio more nearly constant. The integral of (IIA) is

$$\log_e a_{1_{\theta-\mathfrak{J}}} = - (L_\theta/R\theta^2) \cdot \mathfrak{J} \quad . \quad . \quad (IIB)$$

and in point of fact, when the more complicated expressions for the integral of (II) are worked out in full, it is found that the terms involving higher powers of $\mathfrak{J}$ are negligible until depressions of about two degrees are reached. For simplicity therefore we shall neglect them and confine our attention to solutions so dilute that equation (IIB) is adequate.

The variation of $(\bar{F}_1 - F_1^\circ)_{T, \text{const.}} = RT \log_e (a_1/1)$ with temperature follows from equation (6B) from which,

$$d\left(\frac{\bar{F}_1 - F_1^\circ}{T}\right) = (\bar{H}_1 - H_1^\circ) \cdot dT/T^2,$$

where $\bar{H}_1$ is the partial molecular heat content of the solvent in the solution and H_1° is the molecular heat content of the pure liquid solvent. For dilute solutions these two terms are equal, since the thermal effect of adding one gram-molecule of solvent to either pure solvent or a dilute solution is zero, and therefore the activity of the solvent, a_1 , does not vary with temperature so long as this is true. Of course, with concentrated solutions, where there is "heat of dilution," it is not, and a further complication is introduced which also will be disregarded here.

Accordingly, with the limitation that we are dealing only with dilute solutions, the argument can be summed up as follows : The activity of the pure solid solvent, when the pure liquid solvent at the same temperature is assigned unit activity, varies very rapidly with temperature, and its value at any temperature may be calculated from the freezing-point of the pure solvent and the molecular heat of fusion. The activity of the solvent in the solution (also referred to pure liquid solvent at the same temperature) does not vary with temperature. At the freezing-point of the solution the two are equal and therefore the latter may be calculated from the freezing-points of the solution and the pure liquid solvent, and the molecular heat of fusion of the pure solvent. Fig. 3 represents this in diagrammatic form, the ordinates being temperature and abscissæ activity. XQX' represents the activity of the pure liquid solvent, taken arbitrarily as unity at all temperatures. QPR represents the activity of the pure solid solvent, diminishing rapidly with decreasing temperature. Our approximations have represented this as a straight line, whereas, in reality, it is very slightly curved. S'PS represents the activity of the solvent in the solution which is in equilibrium with solid solvent at the temperature $(\theta - \theta')$ as at P. This is represented as independent of temperature, which is true so long as there is no heat of dilution. The slope of the line QPR is given by $(L_\theta/R\theta^2)$, so that when we know the temperature at which the solution is in equilibrium with the solid solvent, we know the point P and hence a_1 .

Take, for example, an aqueous solution with a freezing-point exactly one degree below that of pure water. In this case $\theta = 273$, $L = 1438$ cal., and $\mathcal{J} = 1$.

$$\log_{10} a_1 = (L/2.303R\theta^2)\mathcal{J} = (1438/2.303 \times 1.987 \times 273^2) = -0.004214,$$

and $a_1 = 0.9903$. This will be the ratio of the vapour pressure

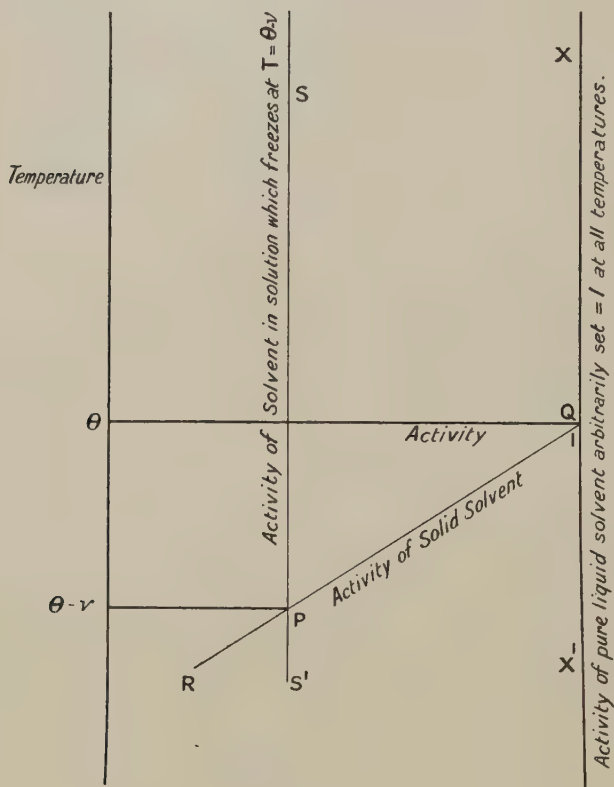


FIG. 3.

of the water from the solution to its value over pure water at any temperature, provided the heat of dilution is negligible.

The variation of the activity of the solute in dilute solution may be determined from freezing-point measurements by combining equations (8A) and (9). From these

$$(d \log_e a_2 = - (n_1/n_2) \cdot d \log_e a_1)_{T, \text{const.}}$$

which, with (IIB) gives,

$$\left(d \log_e a_2 = \frac{n_1 \cdot L_\theta}{n_2 \cdot R \theta^2} \cdot d\vartheta \right)_{T, \text{ const.}} \quad . \quad . \quad . \quad \text{(IIC)}$$

The suffix, $T, \text{ const.}$, can be dropped in the second case because, though we are considering changes in activity due to changes in concentration at constant temperature, for the solutions to which the equation applies the activity is independent of temperature. The depression of the freezing-point, ϑ , is merely an index of the effect of the concentration upon the partial molecular free energy, and does not appear in the conditions under which the change of composition must be conducted.

It has become usual, when making freezing-point determinations, to express the concentration in gram-molecules of solute per 1000 grams of solvent. This is called the "molarity," and is denoted by m . Thus, $n_2 = m$, and $n_1 = 1000/M_1$, where M_1 is the (assumed) molecular weight of the solvent. Consequently it is best to transform the above equation accordingly. It will also be found convenient later to bring the constants together and indicate them by the symbol λ , where $\lambda = (M_1 \cdot R \cdot \theta^2)/(1000 \cdot L_\theta)$, hence

$$d \log_e a_2 = \frac{1000 \cdot L_\theta}{m \cdot M_1 \cdot R \cdot \theta^2} \cdot d\vartheta = \frac{d\vartheta}{m \cdot \lambda} \quad . \quad \text{(IID)}$$

Naturally, the same limitations apply to this as were imposed on equation (IIB) on which it is based, that it applies only to dilute solutions. That it is independent of temperature follows from the application of equation (8) to heat content together with the facts already quoted, for, $n_1 d\bar{H}_1 + n_2 \cdot d\bar{H}_2 = 0$, and since $d\bar{H}_1/dm = 0$ for dilute solution, $d\bar{H}_2/dm = 0$.

The integration of this equation requires that the relation between ϑ and m shall be known over the whole region so that, unlike the case of the activity of the solvent, the activity of the solute in a given solution cannot be obtained from the measurement of the freezing-point of that solution alone. It must be remembered that in these cases the distinction between solute and solvent is not arbitrary, since it is solvent which constitutes the solid phase at the freezing-point. It is often convenient to perform the integration between finite limits graphically, as, for example, by plotting $1/m\lambda$ against ϑ , and measuring the area under the curve. The curve, however, cannot be extrapolated

to zero concentration as then $1/m\lambda$ is infinite, and in any case greater sensitivity may be obtained by mathematical transformation into which it is unnecessary to enter here.

An example is offered by the freezing-point determinations of hydrofluoric acid by Anthony and Hudleston,¹¹ who found that the values for concentrations between 0.1 and 0.5 molar could be expressed by the relation $\vartheta = 1.90m + 0.006$, whence $d\vartheta = 1.90dm$ and

$$\log_e (a_2/a_2') = \int_{0.1}^m (0.90/\lambda m) \cdot dm = 1.023 \log_e (m/0.1),$$

where a_2 is the activity of the hydrogen fluoride in acid of concentration m and a_2' that in 0.1 molar acid, while λ for water was taken as 1.858. For reasons given in the paper they set $a_2' = 0.0876$. Thus, for 0.5 molar acid,

$$\log a_2 = 1.023 \log 5 + \bar{2}.9425 = \bar{1}.6575, \text{ and } a_2 = 0.4534.$$

The choice of some arbitrary value such as a_2' , or the equivalent of *this*, is always necessary in giving numerical values to activities. Had some other value been assigned to a_2' in 0.1 molar solution all the other activities would have been affected in proportion. It is ratios of activities which are determined, and a proportionality factor may always be introduced as equivalent to changing the basic arbitrary choice.

CONVENTIONAL REFERENCE STATES.—Although it is in accord with the definitions given to assign some arbitrary value of activity to a substance in any *one* given state, certain conventions as to the choice have been generally adopted. Two of these have already been mentioned, namely, for gases which may be regarded as perfect $a = p$, and for a liquid solvent (i.e. component of a liquid mixture present in great excess over the others) unit activity is assigned to the pure liquid. The conventions regarding solutes (i.e. components of liquid mixtures present in small proportions) and gases when it is desired to take into account their deviations from the perfect gas law, are similar in principle. The numerical effect in the latter case is usually entirely negligible except at high pressures but, since it illustrates the general principle followed perhaps more simply, it will be considered first.

All gases appear to approach the perfect gas law ever more

closely as the pressure is reduced, and it appears that, at sufficiently low pressure, pV becomes a linear function of p (usually pV at first diminishes as p is increased from zero, then the curve ceases to be even approximately linear, passes through a minimum and finally rises).¹² It is therefore possible at low pressures to express pV by the equation

$$pV = p_0V_0 - \alpha p,$$

where p_0V_0 is the value at zero pressure obtained by extrapolation of the results obtained at very low pressure.

All gases yield the same value of $p_0V_0 = RT$ (kinetic theory), and hence $V = (RT/p) - \alpha$.

The change in molecular free energy, $F - F'$, obtained by compressing one gram-molecule of the gas from p' to p at constant temperature, is given by equation (4) and connected with the change of activity by equation (9A),

$$F - F' = \int_{p'}^p V \cdot dp = RT \log_e (a/a'),$$

and on substituting the above value for V ,

$$RT \log_e (a/a') = RT \log_e (p/p') - \alpha(p - p').$$

If we arbitrarily set $a' = p'$,

$$RT \log_e a = RT \log_e p - \alpha(p - p').$$

It is obviously convenient to choose $p' (= a')$ infinitesimally small when $RT \log_e a = RT \log_e p - \alpha p$.

From this equation it follows that a must approach p ever more closely as the pressure is reduced, and hence there is the advantage that the activity is most nearly numerically equal to the pressure under those conditions where the gas is most nearly perfect.

If the formula appears to hold up to some pressure, p_x , measurable but usually low, at p_x ,

$$\log_{10} a = \log_{10} p_x - (\alpha p_x / 2.303RT) = \gamma \text{ (say).}$$

At higher pressures the formula will sooner or later fail to express the facts, but the activity is obtained from the relation,

$$\log_{10} a = \gamma + \int_{p_x}^p (V/2.303RT) dp,$$

where the last integral, being finite between limits of measurable pressure, may be evaluated graphically. It is often convenient to retain the expression $V = (RT/p) - \alpha$, even above p_x , where α is not taken as constant but has to be determined by experiment, when

$$\log_{10} a = \log_{10} p - \int_{p_x}^p \alpha \cdot dp / 2.303RT.$$

From this illustration it will be clearly seen that the choice of infinitesimally low pressure as the basic reference state requires the adoption of some extrapolation formula by means of which to calculate the numerical value of the activity at some low, but measurable pressure (p_x), and this serves as a practical reference state from which activities at higher pressures may be determined, since it is always possible to obtain the ratio of activities at two measurable pressures if the isotherm of the gas throughout the range between them be known.

The small numerical importance of this convention to gases may be illustrated by the case of nitrous oxide for which Lord Rayleigh found $\alpha = 0.0065$ at 11°C .¹² This value may be taken as constant up to atmospheric pressure without appreciable error, hence, when $p = 1$,

$$\begin{aligned} \log_{10} a &= 0 - (0.0065/2.303 \times 0.08296 \times 284) \\ &= -0.000121 = \bar{1}.999879 \end{aligned}$$

(note that R must be expressed in litre-atmospheres per degree per gram-molecule), and $a = 0.99972$.

With solutes a similar principle is followed. The laws governing solution become simpler as the solution becomes more dilute, so there is a similar advantage in setting $a' = m'$ in the limit when m' is infinitesimally small. For example, the measurements of Brown and Bury¹³ on the depression of the freezing-point of nitrobenzene produced by the addition of benzil (mol. wt. 210.1) are satisfactorily represented by the formula,

$$\Delta = 6.865m - 0.7885m^2,$$

as is seen from the following table, in which x is the number of grams of benzil dissolved in 19.82 grams of nitrobenzene.

x .	m .	$\mathcal{Q}_{\text{obs.}}$	$\mathcal{Q}_{\text{calc.}}$
0.2466	0.0592	0.404	0.404
0.7676	0.1834	1.238	1.238
1.5901	0.3819	2.505	2.506
2.2791	0.5474	3.523	3.522

For concentrations up to half molar,

$$d\mathcal{Q} = 6.865 \cdot dm - 1.5770 \cdot m \cdot dm$$

and $[d\mathcal{Q} = 6.865 \cdot dm]_{\lim m=0}$.

But, since $d \log_e a_2 = d\mathcal{Q}/\lambda m$ and $[a_2 = m]_{\lim m=0}$

$$[m \cdot d \log_e a_2 = dm]_{\lim m=0}$$

and $[d\mathcal{Q} = \lambda \cdot dm]_{\lim m=0}$.

Thus, in the present case, $\lambda = 6.865$ and

$$d \log_e a_2 = d \log_e m - 0.2298m \cdot dm$$

integrating and converting into ordinary logarithms,

$$\log_{10} a_2 = \log_{10} m - 0.0449m^2.$$

When $m = 0.5$, $\log_{10} a_2 = \bar{1}.6868$, and $a_2 = 0.486$.

At higher concentrations the formula might no longer hold and the activity is obtained from the expression

$$\log_{10} a_2 = \bar{1}.6865 + \int_{0.5}^m d\mathcal{Q}/\lambda m,$$

where the integral may be evaluated graphically if necessary, being finite between measurable limits.

The same principle again holds good. To gain the advantage of having the numerical values of activity ever more closely approaching those of the molarity as the solution becomes more and more dilute the basic reference state must be the infinitely dilute solution. But, as this is inaccessible to measurement, it is necessary to adopt some extrapolation formula which is assumed to hold over the whole range from low to zero concentration and calculate by means of this the activity in some measurable concentration to serve as a practical reference basis. From this point onwards the activities are determined as explained in the previous section. The general principle is just the same when any other method, such as the vapour pressure method, is employed to determine activities.

In the case of solutes it is comparatively rare to find a formula which will hold up to concentrations as high as this. Moreover, even the type of formula which can be applied varies from case to case, that given in the illustration being one of the simplest. Further discussion of suitable formulæ will be found in the sections on perfect solution and on the treatment of strong electrolytes. In all cases it must be clearly understood that there is nothing absolute about values of activity calculated in this manner, for, however closely a given formula may represent the facts in dilute solution, the assumption that it holds through the range inaccessible to measurement down to zero concentration is an act of faith.

Whilst the basic reference state of a solute is that in which its activity is infinitesimal, the free energy changes of reactions are tabulated on the basis that each substance taking part is at unit activity. This, however, does not introduce any real difficulty, being comparable with the use of a graph on such a scale that the zero does not appear on the paper. Again, an example with a gas is helpful. At 100° C., $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ are together in equilibrium with water vapour at 688 mm. pressure (0.905 atm.).¹⁴ Taking the activity of the pure solids as unity and that of the vapour as equal to its pressure (i.e. assuming the vapour to be perfect), for the reaction

$$\text{CuSO}_4 \cdot 3\text{H}_2\text{O}(a = 1) + 2\text{H}_2\text{O}(g, a = 0.95) \\ = \text{CuSO}_4 \cdot 5\text{H}_2\text{O}(a = 1), \Delta F_{373} = 0,$$

since equilibrium exists. By equation (10), for the reaction between the substances all at unit activity,

$$\Delta F_{373}^0 = 0 + RT \log_e (0.95)^2 = -15 \text{ cals.},$$

representing the free energy change when one gram-molecule of solid copper sulphate trihydrate reacts at 100° C. with two gram-molecules of water vapour at unit activity to form one gram-molecule of solid copper sulphate pentahydrate. Here water vapour at unit activity is represented physically by the vapour at unit pressure if the gas law is assumed, or at some very slightly higher pressure (supersaturated) if the imperfections are taken into account. But at 25° C. the equilibrium pressure is only 8.5 mm. (0.0112 atm.). The same formal method of expression and calculation is adopted, and

$$\Delta F_{298}^0 = RT \log_e (0.0112)^2 = -5324 \text{ cals.},$$

meaning that this is (or would be) the free energy change resulting from the reaction between one gram-molecule of copper sulphate trihydrate at 25°C. with two gram-molecules of water vapour at unit activity to form one gram-molecule of copper sulphate pentahydrate. But in this case it is physically impossible to have water vapour present at unit activity, since the vapour would be condensed at this temperature before the necessary pressure could be applied. This makes no difference to the usefulness of the numerical value of ΔF_{298}° which may be employed, in conjunction with equation (10), to give correct values for the free energy change of the reaction with water vapour at any physically possible activity. Thus, in this case "water vapour at unit activity" constitutes merely a convenient mathematical zero (of molecular free energy) defined indirectly but quite rigidly in very much the same way as the absolute zero of temperature is defined, although physically unattainable.

Similarly, the limits of solubility may prevent solutions of unit activity being physically possible without impairing the convenience of the concept for purposes of tabulation.

The example given should have prepared the reader to realise that, even in cases where unit activity is physically attainable, the particular state required may vary with temperature. If $\bar{F}$ and $\bar{F}'$ represent the partial molecular free energy of a solute at two different concentrations, m and m' , in which the activity is denoted by, respectively, a and a' , from equations (6B) and (9)

$$d\left(\frac{\bar{F}}{T} - \frac{\bar{F}'}{T}\right) = R \cdot d \log_e (a/a') = (\bar{H} - \bar{H}')/T^2 \cdot dT,$$

where $\bar{H}$ is the molecular heat content. If m' represents an infinitesimal concentration, $a' = m'$ at all temperatures by the conventional choice of basic state. Consequently, the activity, a , corresponding to any given concentration m , must change with temperature if $\bar{H}$ differs from $\bar{H}'$. This last point may be determined by dissolving one gram-molecule of the solute in an infinite quantity of solution of concentration m (or arriving at this figure by a mathematical treatment similar to that employed in determining the partial molecular volume) and comparing the result with that obtained from a similar experiment with pure solvent (infinitesimal concentration, m'). The difference is $\bar{H} - \bar{H}'$ and will, in general, be appreciable

when m is sufficiently large to give solutions of about unit activity for the solute. Consequently, in general, the activity at any given concentration varies with temperature and so the concentration at which any given activity is attained must also vary with temperature.

It must be remembered that activities are fundamentally relative quantities referring to the same temperature. The activity of the solute at m and T_1 is measured with reference to that at m' and T_1 , while the activity at m and T_2 is relative to that at m' and T_2 . We cannot really measure the fundamental relation between the activities at m and T_2 and at m and T_1 because we do not know how the activity at m' and T_2 compares with that at m' and T_1 . It is an arbitrary choice which assigns the value $a' = m'$ at both temperatures.

G. N. Lewis uses the concept of a condition called the "standard state" in which the activity is unity (on the conventions given) and the heat content the same as that for the basic reference state, and defines ΔF° as the free energy change of the reaction between the substances in their standard states. For solids, pure liquids, solvents, and gases which may be regarded as perfect, the standard state is simply the pure substance at atmospheric pressure, while for solutes and imperfect gases the condition may be purely hypothetical.

Lastly, it should be pointed out that the basic reference state of a solute is specific to each solvent. This may be illustrated by the simple case of a solute which obeys Henry's law at great dilution in several solvents. For each, $[p = bm]_{\lim m = 0}$ where b is a constant for any one solvent but varies from case to case, according to the constraining forces between the molecules. But, by convention, $[a = m]_{\lim m = 0}$ and, if the vapour of the solute be regarded as a perfect gas, the partial vapour pressure will be proportional to the activity at all concentrations, so $p = ba$. Therefore, in each solvent, unit activity will be attained when the partial pressure of the solute is b , the value of which is specific to the solvent in question.

LAW OF PERFECT SOLUTION.—The simplicity of the treatment of perfect gases has its origin in the absence of any physical attraction between their molecules so that each species may be treated as if it alone were present, and real gases approach fairly closely to this condition. In liquid solutions, however, the

cohesive forces between the molecules must be enormous and usually highly specific, and in consequence any law of "perfect solution," corresponding to the perfect gas law, is likely to be approached more rarely. The form of such a law may be deduced from the consideration of the simplest possible case, a binary mixture in which the constraining forces are the same for both species of molecules and independent of the proportions of the components. In such a case it would be expected that the total vapour pressure would be independent of the composition, and that the composition of the gaseous and liquid phases would be the same. But in this case the partial pressures of the components in the vapour would be proportional to the molar fraction (since the total pressure is constant), which would also be the molar fraction in the solution.

Experiment confirms this postulate. Zawidski¹⁵ carried out a series of determinations of the partial pressures with binary mixtures of organic liquids at constant temperature and found that the more nearly the components resembled each other in chemical and physical properties, the more nearly was the partial pressure of each proportional to the molar fraction in the liquid. As an example, the favourable case of mixtures of benzol and ethylene chloride (at 50° C.) may be quoted. If P , p , and N denote, respectively, the vapour pressure in the pure state, the partial vapour pressure over the mixture, and the molar fraction, the substance referred to being indicated by a suffix, the above law requires that $p_1 = N_1 P_1$ and $p_2 = N_2 P_2$, whence

$$(p_1/p_2)/(N_1/N_2) = P_1/P_2 = k \text{ (a const.)}.$$

The following table summarises the results obtained, alternative figures for k corresponding to duplicate measurements:—

N_2	0.1500	0.2927	0.4156	0.6566	0.7542	0.9206
k {	0.738	0.866	0.888	0.878	0.879	0.872
	0.826	0.896	—	0.876	0.884	—

The mean value (including some results not quoted here) for k was 0.880, whilst $P_1/P_2 = 0.881$. In this case the law evidently holds good within the limits of experimental error but, as is only to be expected, in the majority of cases very great departures are to be observed.

Treating the components separately, the essential condition appears to be that the constraining forces on the molecules should be constant and independent of the composition. This condition is likely to be nearly realised in the case of very dilute solution where each molecule of solvent is surrounded almost entirely by its fellows and hence is practically subject to the same constraint as in the pure solvent, the rare solute molecule exerting but little influence on the general inter-molecular field of force. Similarly, the solute molecule is surrounded almost entirely by molecules of the solvent, the intrusion of another solute molecule into the region of molecular attraction being rare when the dispersion is high, and so the constraining forces will be hardly affected by concentration (while this remains low) though they may be very different from those ruling in the pure solute. In mathematical language, if the effect of the solute on the inter-molecular field of force be of a lower order of magnitude than its effect on the molar fraction (which is frequently, though not necessarily always, the case) the solution will approach perfection as it becomes more and more dilute.

This has been recognised in many empirical laws of dilute solution. For example, Raoult's law of vapour pressures state that, if p_0 be the vapour pressure of the pure solvent, and p be the vapour pressure of the solvent over a solution containing n_2 gram-molecules of solute and n_1 gram-molecules of solvent, then $(p^\circ - p)/p^\circ = n_2/(n_1 + n_2)$. Subtracting 1 from each side of this equation we obtain $p = N_1 p^\circ$, showing that the law is only a special case of the general law of perfect solution given above.

We have seen that, if the molecular weight of the substance as a liquid be taken as that which the substance shows (from the gas law) as a gas, the vapour pressure is proportional to the activity, so the law of perfect solution may be put in the form that the activity is proportiona to the molar fraction. For the solvent in dilute solution it is convenient to assign unit activity to the pure substance, so $a_1 = N_1$ when Raoult's law is obeyed.

With regard to the second component, an interesting relation follows from the application of equation (8A). On substituting $RTd \log_e a$ for $d\bar{F}$, for changes due to variation in the proportions of the components only, the temperature being constant,

$$d \log_e a_1 = - (n_2/n_1) d \log_e a_2 = - (N_2/N_1) d \log_e a_2,$$

but if $a_1 = N_1$, $N_1 d \log_e a_1 = dN_1$ and, since $N_1 + N_2 = 1$,
 $dN_1 = -dN_2$,

therefore $dN_2 = N_2 d \log_e a_2$, whence a_2 is proportional to N_2 . Thus, if the solution is perfect with respect to the solvent, it must also be perfect with respect to the solute, the criterion of perfection being that the activity is proportional to the molar fraction.

As in the case of gases the question of the chosen molecular weight arises when considering whether a solution is perfect or not, for on this the molar fraction depends. There is also the possibility of disturbance by chemical reaction such as dissociation or solvation. The idea still persists, although apparently definitely erroneous in some cases, that all solutions are sensibly perfect at considerable dilution if correct molecular weights be employed and allowance made for chemical reaction so as to get the "true" molar fraction of the solvent. Let us follow out this idea with reference to freezing-point measurements. By equation (IIB), $\log_e a_1 = - (L/R\theta^2) \cdot \mathfrak{J}$. If $a_1 = N_1'$, where N_1' is the "true" molar fraction of the solute, since $N_1' = (1 - \Sigma N_2')$, where $\Sigma N_2'$ equals the sum of the molar fractions of all the molecular species actually present which are not pure solvent, and $\log_e (1 - \Sigma N_2') = - \Sigma N_2'$ by the well-known approximation when $\Sigma N_2'$ is small, we have $\mathfrak{J} = (R\theta^2/L) \cdot \Sigma N_2'$. To connect this with measured quantities let W_2 represent the number of grams of solute dissolved in 1000 grams of solvent, then

$$m = W_2/M_2$$

is the formal molarity, where M_2 is the assumed molecular weight of the solute. If we define $n_1 = 1000/M_1$, where M_1 is the assumed molecular weight of the solvent, then $\Sigma N_2' = x/(n_1 + y)$, where x is the "true" number of gram-molecules of substance other than pure solvent present per thousand grams of solvent and y is a quantity such that $(n_1 + y)$ equals the "true" total number of gram-molecules of all species present per thousand grams of solvent. Expanding this into a series,

$$\Sigma N_2' = (x/n_1) - (xy/n_1^2) + (xy^2/n_1^3) - \dots$$

of which the higher members may be neglected for dilute solution $\mathfrak{J} = \lambda x - (\lambda xy/n_1)$, where $\lambda = M_1 R \theta^2 / 1000L$ as before, or

$$\mathfrak{J}/m = \lambda(x/m) - \lambda(xy/mn_1).$$

If correct molecular weights have been employed and there is no chemical reaction, $x = y = m$, and

$$\mathcal{D}/m = \lambda - \lambda m/n_1 = \lambda - \lambda m M_1/1000,$$

and the plot of $\mathcal{D}/m$ will be linear with a downward slope as m increases. This differs from the usual assumption that $\mathcal{D}/m$ should be constant and equal to λ but in actual practice it is found that all freezing-point determinations with so-called normal organic substances show such a slope. Brown and Bury¹³ found that the freezing-point depression is proportional to the molar fraction for several solutes in nitrobenzene up to remarkably high concentrations, while Washburn and Read,¹⁶ using the same basic assumption, were able to calculate with considerable accuracy the eutectic points of various mixtures. If $\mathcal{D}/m$ were constant it would follow from equation (IID) that the activity of the solute was proportional to the molarity, an assumption that has been employed in countless calculations, but the present author is not aware of a single case for which the data support that assumption in preference to the proportionality to the molar fraction adopted in this work (though both fail completely in many instances). The slope of the curve is proportional to the molecular weight of the solvent, and hence is more apparent the greater this may be.

The equation shows that a false molecular weight of the solvent does not affect the limiting value of $\mathcal{D}/m$ since L is the heat of fusion of the assumed molecular weight of the solvent, so L/M_1 and λ are therefore independent of the choice of M_1 . The slope of the line, however, would indicate the molecular weight of the solvent if the data were sufficiently accurate, were it not for the fact that this is also affected by solvation.

On the other hand, an inaccurate molecular weight of the solute is at once detected, since in that case $x = y = fm$, where f is some factor, and $\mathcal{D}/m = f\lambda - f^2\lambda m/n_1$, so that even the limiting value of $\mathcal{D}/m$ (when $m = 0$) is affected. Hence, as is well known, freezing-point determinations are available to determine the molecular weights of substances in solution.

If solvation occurs, each molecule of solute combining with b molecules of solvent, $x = m$, but the total number of gram-molecules of all species present is $n_1 - b \cdot m + m$, so

$$y = n_1 + (1 - b)m.$$

Consequently, $\mathcal{G}/m = \lambda - (1 - b)\lambda m/n_1$ and the limiting value is unaffected, though the slope is altered.

Innumerable other cases might be worked out and the plot of $\mathcal{G}/m$ against m drawn. If in any given case the experimental data fit on some such curve there is fair reason to believe that the abnormality has been "explained" by the chemical reaction assumed. If the reaction be very complicated, however, such as Drucker and Riethof¹⁷ assume for strong electrolytes, where they postulate the presence of several complex ions, several constants will be introduced into the calculation, and as almost any curve can be satisfactorily represented if there are three or four arbitrary constants to be introduced, agreement in such a case would not necessarily indicate anything more than mathematical dexterity.

The case where the "perfect" law is obscured by dissociation is of some importance, and may be illustrated by reference to the typical case of nitrogen peroxide. The variation with pressure of the molecular free energy of this gas determined by the integration of $V \cdot dp$ would be abnormal for any chosen molecular weight because the isotherm is abnormal. The results are, however, in fair agreement with the theory that, owing to the reaction $N_2O_4 = 2NO_2$, we are really dealing with a gaseous equilibrium in which each gas individually may be regarded as perfect. According to this, 92 grams of the substance would contain $(1 - \alpha)$ gram-molecules of N_2O_4 and 2α gram-molecules of NO_2 , where α is said to be the fraction dissociated and is determined from the equation $pV = (1 + \alpha)RT$, if V is the volume containing 92 grams and each gas individually is supposed to be perfect. But this assumption also requires that the activity of each gas separately shall be proportional to its partial pressure, and consequently that $4\alpha^2 P / (1 - \alpha^2)$, where P is the total pressure, should be constant at constant temperature. This appears to be the case from Schreber's¹⁸ figures, as shown in the table below. Densities are given relative to air, making that for pure N_2O_4 3.876. The temperature was 0° C.

P mms.	$d.$	α .	K.
37.96	2.483	0.2856	13.48
86.57	2.674	0.1877	12.64
172.5	2.820	0.1262	12.54
250.7	2.903	0.0941	8.96

The last pressure was somewhat too close to the vapour pressure of the liquid.

The important point is that, if the theory is correct and the departure from the perfect gas law is due solely to dissociation, the free energy of any given quantity of the substance would be the same whether it existed as equilibrium mixture at a total pressure P or as pure NO_2 at p_s or as pure N_2O_4 at p_a , where p_s and p_a are, respectively, the partial pressures of NO_2 and N_2O_4 in the equilibrium mixture at P . Thus, on changing the total pressure of a given mass from P to P' the free energy change is

$$\int_P^{P'} V \cdot dP = \int_{p_a}^{p_a'} V \cdot dp_a = \int_{p_s}^{p_s'} V \cdot dp_s = x \cdot RT \cdot \log_e (p'/p),$$

where x is the number of gram-molecules concerned and p is the partial pressure of that gas from the molecular weight of which x was determined. This is not obvious at first sight because, for example, pure N_2O_4 would tend to dissociate at any pressure, but that is only because it thereby tends to lower its own partial pressure. If it were introduced into a practically infinite amount of equilibrium mixture at P it would exist with the remainder of the N_2O_4 at partial pressure p_a without dissociation.

The actual integration may prove a useful help. If V_{92} is the volume containing 92 grams and each gas considered separately is perfect, $V_{92} \cdot dP = (1 + \alpha) \cdot RT \cdot dP/P$,

but $K \cdot p_a = p_s^2$, whence $p_s = K\sqrt{p_a}$

$$P = p_a + p_s = p_a + K\sqrt{p_a}$$

$$dP = dp_a + (K/2\sqrt{p_a})dp_a = [(2\sqrt{p_a} + K)/2\sqrt{p_a}]dp_a$$

again $p_a/P = (1 - \alpha)/(1 + \alpha)$, whence $\alpha = K\sqrt{p_a}/(2p_a + K\sqrt{p_a})$.

Combining, $V_{92} \cdot dP = RT \cdot dp_a/p_a$, so

$$\int_P^{P'} V_{92} \cdot dP = RT \log_e (p'_a/p_a).$$

If the volume, V_{46} , be taken corresponding to 46 grams,

$$V_{46} = V_{92}/2 \text{ and } \int_P^{P'} V_{46} \cdot dP = \frac{1}{2} RT \log_e (p'_a/p_a) = RT \log_e (p'_s/p_s).$$

Thus, whichever molecular weight be chosen, the change of free energy per (assumed) gram-molecule with pressure is given

by $RT \log_e (p'/p)$, where p is the partial pressure of the gas having the assumed molecular weight. This result is perfectly general and applies to all cases, gaseous or liquid (solution), in which the departure from the "perfect" law is due *solely* to a change in the number of molecules due to reversible chemical reaction. Conversely, if the total free energy be measured it may be employed to determine the variation of partial pressure of the component which has the molecular weight chosen to represent the substance as a whole, *if each component separately obeys the perfect gas law*. Applied analogously to solutions this opens up a possible means of determining the extent of dissociation which has been widely applied in dilute solution where, until recently, it was implicitly assumed that the activity would always be proportional to the true molarity—an assumption which, as we shall see, may be quite erroneous.

ELECTROLYTES.—According to the law of the independent mobility of ions put forward by Kohlrausch, the fraction of an electrolyte that is dissociated is given by $\alpha = \lambda_v/\lambda_\infty$, and thus the true concentrations of the ions and undissociated molecules could be determined. Arrhenius checked this postulate by applying the law of mass action, which makes the assumption that the activity of each species is proportional to its concentration. As is well known, with weak electrolytes a good constant was obtained but strong electrolytes gave anomalous results. It therefore became of great interest to determine whether this anomaly was due to any failure of the law of Kohlrausch or to that of the law of mass action itself, or perhaps to both. Thermodynamic methods are capable of throwing a little light on the latter, at least in so far as the change in the number of the molecules is supposed to be due only to dissociation, and the vast amount of attention accorded to the study of strong electrolytes in recent years justifies a detailed consideration of the methods adopted in applying equation (IID) to them, the essential problem being that of integration from zero to concentrations readily accessible to experimental measurement. In all cases $\mathcal{G}$ appears to approach $\eta\lambda m$ in the limit $m = 0$, where η is an integral number equal to the number of ions into which the electrolyte dissociates. Hence $[d\mathcal{G} = \eta\lambda dm = \lambda m \cdot d \log_e a_2]_{m=0}$,

or $[d \log_e m = d \log_e a_2^{1/\eta}]_{m=0}$ and $[m = a_2^{1/\eta}]_{m=0}$.

It is therefore more convenient to divide equation (IID) by η giving

$$d \log_e a_2^{1/\eta} = d\mathfrak{A}/\eta\lambda m \quad . \quad . \quad . \quad \text{(IIE)}$$

from which, with the relation given above,

$$[d \log_e a_2^{1/\eta} = d \log_e m]_{m=0}.$$

The significance of $a_2^{1/\eta}$ is best shown in an example, e.g. sulphuric acid. Since dissociation occurs according to the reaction $\text{H}_2\text{SO}_4 = 2\text{H}^+ + \text{SO}_4''$ we have $kx a_{\text{H}_2\text{SO}_4} = a_{\text{H}^+}^2 + a_{\text{SO}_4''}$. At infinite dilution we may set the activities of the ions equal to their stoichiometrical molarities, which will be $2m$ and m respectively. But we know nothing about the concentration of the undissociated molecules under any conditions and cannot follow the same procedure in this case. Since numerical values of activity may always be multiplied by a common factor by changing the value for the basic reference state it is quite permissible to choose such a value that $k = 1$ in the above equation, when the activity of the undissociated molecules is given simply by $a_{\text{H}^+}^2 \times a_{\text{SO}_4''} = a_{\text{H}_2\text{SO}_4} = a_2$. Then $a_2^{\frac{1}{2}} = \sqrt[3]{(a_{\text{H}^+}^2 \times a_{\text{SO}_4''})}$ called the "mean activity" and denoted by $a_{\pm}$. In general, $a_{\pm} = a_2^{1/\eta}$. For any substance for which the basic reference state is $[a = m]_{m=0}$ the activity divided by the stoichiometrical molarity is called the "activity coefficient," denoted by γ . Thus, in the present case, $\gamma_{\text{H}^+} = a_{\text{H}^+}/2m$ and $\gamma_{\text{SO}_4''} = a_{\text{SO}_4''}/m$. The so-called "activity coefficient" of the electrolyte as a whole, γ , is really a mean activity coefficient obtained in the same way as the mean activity, and should be denoted by $\gamma_{\pm}$ for the sake of consistency. By convention, however, the subscript is usually dropped. For sulphuric acid

$$\gamma \text{ (or } \gamma_{\pm} \text{ or } \gamma_{\text{H}_2\text{SO}_4}) = (\gamma_{\text{H}^+}^2 \times \gamma_{\text{SO}_4''})^{\frac{1}{3}} = a_{\pm}/m \cdot \sqrt[3]{4}.$$

In the simplest case, a binary electrolyte,

$$\gamma = a_{\pm}/m = \sqrt{a_2}/m.$$

A more complicated example is afforded by Na_2HPO_4 , where $\gamma^4 = (a_{\text{Na}^+}/2m)^2(a_{\text{H}^+}/m)(a_{\text{PO}_4''}/m)$ or

$$\gamma = a_{\pm}/m \sqrt[4]{4} = \sqrt[4]{a_2}/m \sqrt[4]{4}.$$

In all cases

$$d \log_e \gamma = d \log_e a_{\pm} - d \log_e m = d \log_e (a_{\pm}/m)$$

and, by the definition of the basic states of reference of the ions $[\gamma = 1]_{m=0}$.

Returning now to equation (IIE), we have seen that $\mathfrak{J}/\eta\gamma m$ approaches 1 in the limit as the concentration is indefinitely reduced. Consequently the function, $J = 1 - (\mathfrak{J}/\eta\gamma m)$ should be useful for extrapolation since it becomes zero in the limit.

By calculus,

$$dJ = \frac{-\eta\gamma m \cdot d\mathfrak{J} + \eta\gamma \mathfrak{J} \cdot dm}{(\eta\gamma m)^2} = - (d\mathfrak{J}/\eta\gamma m) + (\mathfrak{J}/\eta\gamma m)(dm/m)$$

Substituting into equation (IIE) and subtracting $\log_e m$ from both sides, and noting the $\mathfrak{J}/\eta\gamma m = 1 - J$,

$$d \log_e (a_{\pm}/m) = d \log_e \gamma = -dJ - J \cdot d \log_e m \quad \text{(IIF)}$$

Integration gives $2.303 \log_{10} \gamma = -J - \int_0^m (J/m) \cdot dm$, since

$J = 0$ when $m = 0$. As J/m is an extremely sensitive function, the remaining integral may be determined graphically between suitable finite limits, but the sensitivity is too great for reliance to be placed on results at very low concentration where the experimental errors are necessarily somewhat high in proportion to the total depression. Moreover, J/m approaches infinity as the solution approaches zero concentration. Consequently, it is necessary to adopt some extrapolation formula to effect the integration from zero to some low concentration, $m = 0.01$ say, at which experimental results are reliable. That most widely adopted was put forward by Lewis and Linhart¹⁹ and assumes that, below 0.01 molar, $J = \beta m^\alpha$, where the constants α and β are obtained empirically by plotting $\log_{10} J$ against $\log_{10} m$, the slope giving α and the intercept on the axis $m = 0$ (obtained by linear extrapolation) is β . The results at low concentration serve to establish this line, although the very lowest figures have usually to be neglected as unreliable. It follows that

$$\int_0^m (J/m) \cdot dm = \int_0^m (\beta m^{\alpha-1}) \cdot dm = (\beta m^\alpha)/\alpha = J/\alpha.$$

Before illustrating this method a neat alternative due to Randall²⁰ may be explained. He plots $J/\sqrt{m} = B$ (say) against $\sqrt{m}$, because experiment seems to show that B remains finite

even down to zero concentration, at which its value may be denoted by B_0 . Equation (IIF) is then suitably transposed,

$$dJ = B \cdot d\sqrt{m} + \sqrt{m} \cdot dB,$$

$$\text{and } J \cdot d \log_e m = (J/m) \cdot dm = (B/\sqrt{m}) \cdot dm = 2B \cdot d\sqrt{m},$$

$$\text{therefore } d \log_e \gamma = -3B \cdot d\sqrt{m} - \sqrt{m} \cdot dB.$$

If, from zero concentration up, B remained constant, the integral would be $\log_e \gamma = -3B_0\sqrt{m}$, and even if B varies, so long as it remains finite this relation will still be approached in the limit $m = 0$. It may be compared with the relation

$$\log_e \gamma = -Aw' \cdot \sqrt{m}$$

deduced by Debye and Hückel²¹ from their theory, based on kinetic considerations, taking into account the mutual effect of the charges on the ions, in which A is calculated from the dielectric constant of water and other fundamental constants and w' , also calculable, depends only upon the valence type of the electrolyte. Controversy still rages about this theory, but it is generally admitted to be correct in the limiting case of zero concentration, whence $B_0 = Aw'/3$ and is calculated without reference to the freezing-point data. This allows the graph of B against $\sqrt{m}$ to be drawn without undue reliance upon the probably erroneous figures at very low concentrations. In order to obtain γ it is most convenient to work with the partial transformation of equation (IIF),

$$d \log_e \gamma = -dJ - \int_0^m 2B \cdot d\sqrt{m}$$

which yields

$$\log_{10} \gamma = - (J/2.303) - 2X/2.303,$$

where X is obtained by the graphical integration of $B \cdot d\sqrt{m}$.

The value of B_0 for the difference valence types are given by Randall as follows :—

uni-uni.	uni-bi.	uni-tri.	bi-bi.	bi-tri.
0.375	1.300	2.760	3.00	8.73

These two methods may be illustrated with reference to the data of Randall and Vanselow²² on the freezing-points of hydrochloric acid. The pertinent data are given in the following table :

m .	$\sqrt{m}$.	J.	B.
0.0006270	0.02505	0.01615	0.6407
0.0012448	0.03529	0.01682	0.4767
0.0018208	0.04268	0.01329	0.3114
0.0035261	0.05937	0.01816	0.3059
0.005210	0.07219	0.02279	0.3157
0.008573	0.09260	0.02787	0.3010
0.013258	0.1151	0.03317	0.2881
0.051633	0.2273	0.04721	0.2077
0.050063	0.2238	0.04647	0.2077
0.070563	0.2658	0.05091	0.1916

From the plot of $\log_{10} J$ against $\log_{10} m$ the authors deduce $J = 0.316m^{0.513}$ so that, when $M = 0.01$, $J = 0.02976$ and $\log_{10} \gamma = - (0.0296/2.303) - (0.02976/2.303 \times 0.513) = -0.0381$ and $\gamma = 0.916$.

For the second method the present author has drawn the curve of B against $\sqrt{m}$, as shown in Fig. 4. It is almost linear from $B_0 = 0.375$ (by theory) at $\sqrt{m} = 0$ to $B = 0.280$ when $\sqrt{m} = 0.1$, making $J = 0.0280$ when $m = 0.01$ and

$$\int_0^{0.01} B \cdot d\sqrt{m} = 0.3275.$$

Consequently, when $m = 0.01$,

$\log_{10} \gamma = - (0.0280/2.303) - (2 \times 0.03275/2.303) = -0.0406$ and $\gamma = 0.911$.

The numerical difference is thus seen to be small, although the basic assumptions are really fundamentally different. Criticism as to the relative merits of the systems is beyond the scope of this work since, from the point of view here developed, it does not matter which value be adopted so long as the same practical reference state is given, on any convention, a common value for γ (and therefore for a_2) by different authorities. The values soon to be published in International Critical Tables will doubtless provide this common convention. They will also give a complete survey of the activities so far determined which are too numerous for inclusion here.

If the law of mass action applied and the change in the number of the molecules were due solely to dissociation, for a binary electrolyte $\gamma m = a_{\pm}$ should represent the true molarity of each ion and $m - \gamma m$ that of the undissociated molecules.

Consequently, $\gamma^2 m / (1 - \gamma)$ should give a constant, but this is not found to be the case for strong electrolytes. Moreover, the extrapolation formulæ that have been discussed are incompatible with these two assumptions. In any case the second assumption is probably invalidated by solvation but also the

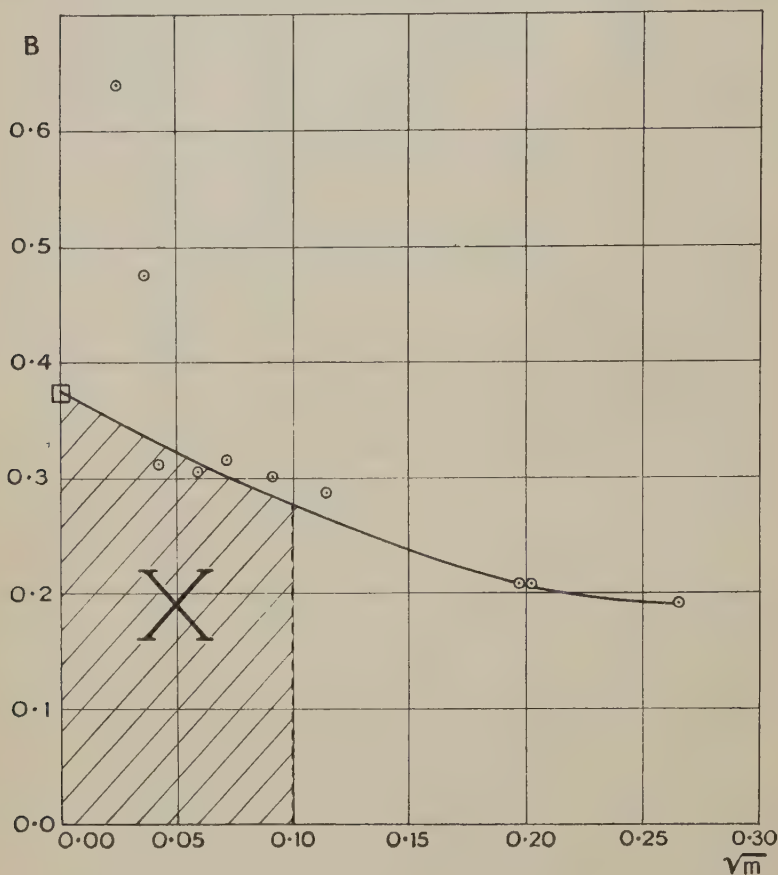


FIG. 4.

modern theory of electrolytes takes account of the mutual effect of the charges on the ions and deduces from this that the activity of an ion shall not be proportional to its true concentration on account of the influence of its neighbours. Incidentally it is also deduced that the mobilities of the ions are not independent of the concentration.

The effect of this on weak electrolytes has only very recently been considered. The fact that the "concentrations" of the ions and undissociated molecules calculated from conductivity data gave a constant in the mass law equation suggested that, unless some curious compensation of errors existed, they must be proportional to the activities. Hence it was convenient to set the activities equal to these concentrations. Electromotive force measurements on hydrofluoric acid, carried out under the author's direction,²³ showed that the activity of the hydrogen ion remained proportional to its concentration as calculated from conductivity (when due allowance was made for complex ion formation)²⁴ up to molar concentration. On the other hand, Jones and Bury²⁵ have recently found from measurements of freezing-points that the activity of acetic acid in aqueous solution is not proportional to its concentration as deduced from conductivity measurements (which is very nearly the same as its stoichiometrical concentration). In the absence of any suitable extrapolation formula these authors have had to content themselves with assigning an arbitrary value of activity to the acid in some one concentration. The subject obviously offers a wide scope for enquiry.

ACTIVITY AND ELECTROMOTIVE FORCE.—The practical use of activities lies in their application by means of equation (10) to the free energy changes of reactions in solution at different concentrations. Consider the equation,



As it stands it is not precise and the free energy change associated with it can be written only in the form

$$\Delta F = \Delta F^\circ + RT \log_e \frac{a_{\text{HBr}} \times a_{\text{Ag}}}{a_{\text{H}_2}^{\frac{1}{2}} \times a_{\text{AgBr}}}$$

where ΔF° is the free energy change resulting when all the substances considered are in their standard states. The two solids, if pure, have practically constant molecular free energy at constant temperature, so their activity will remain unity, but the chemical affinity will be profoundly affected by the pressure of the hydrogen and the concentration of the acid. The system may be set up in the form of a galvanic cell and the driving force counterbalanced by an electromotive force E , or E° for the

case that all the substances are at unit activity. If the reaction proceeds to the extent of the quantities indicated in the equation one faraday will pass through the cell from the negative to the positive electrode (and externally, of course, from the positive to the negative electrode). Consequently, as has been shown,

Chemical affinity = $-\Delta F = E$ volt faradays = 23060 E cals., or, $E = E^\circ - (2.303RT/f) \log_{10} (a_{\text{HBr}}/a_{\text{H}_2}^{\frac{1}{2}})$.*

The value of E having been determined for any one set of conditions for which the activities of the hydrogen and the acid were known, E° or E for any other conditions of known activity relations may be readily calculated. At 25° C., RT in joules is 8.316×298 and f is 96,500 coulombs, so at this temperature,

$$E = E^\circ - 0.0591 \log_{10} (a_{\text{HBr}}/a_{\text{H}_2}^{\frac{1}{2}}).$$

The effect of variations in the pressure of the hydrogen alone, the concentration of the acid remaining constant, is readily calculated since the activity may be taken as equal to the pressure. Thus, doubling the pressure decreases the ratio in brackets in the proportion $1 : \sqrt{2}$ and therefore alters the equilibrium electromotive force by

$$- 0.0591 \log_{10} (1/\sqrt{2}) = + 0.0089 \text{ volts.}$$

Similarly, if the hydrogen pressure is kept constant (or a suitable correction made as above) while the concentration of the acid is varied, we may calculate the ratio of the activities in the two solutions from the measured values of the electromotive force or, if the ratio of the activities and the electromotive force in one case be known, we may calculate the electromotive force in the other case. For example, Livingston²⁶ found that with 0.0850*m* acid the electromotive force was 0.2101 volts and with 1.010*m* acid it was 0.0804 volts, the hydrogen being at atmospheric pressure in both cases. Consequently, $E - E' = 0.0591 \log_{10} (a_2/a_2')$ whence $a_2/a_2' = 15.7$. This is a very convenient method of determining the activity of an electrolyte in moderate and concentrated solution, since the electromotive force equation is exact while the freezing-point equation in the simple form here employed is only approximate and, though adequate in dilute solution, becomes more complicated if it is to be employed at higher concentrations. It is thus easy to find the activity of a dilute solution by the freezing-point

* $RT = 8.315 \text{ T joules.}$

method and to extend the measurements to higher concentrations by determinations of electromotive force.

Where the electrical measurements extend to sufficiently low concentrations of the acid, as is the case in the analogous cell, $\text{H}_2(\text{g. } 1 \text{ atm.}), \text{HCl aq.}, \text{AgCl(s)}, \text{Ag}$,²⁷ direct extrapolation may be made with these and the preliminary determination by freezing-point measurements dispensed with. The simplest method is due to Lewis.³ By transforming the equation to

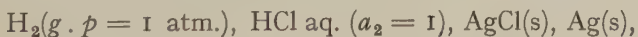
$$E^\circ - E = + 0.1182 \log_{10} (a_{\pm}/1),$$

subtracting $0.1182 \log_{10} m$ from both sides and rearranging,

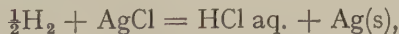
$$0.1182 \log_{10} (a_{\pm}/m) = 0.1182 \log_{10} \gamma = E^\circ - (E + 0.1182 \log_{10} m).$$

The term in brackets consists entirely of measured values and may be plotted against $\sqrt{m}$ (since $\log \gamma$ is proportional to $\sqrt{m}$ in very dilute solution, thus giving a linear graph). This may be extrapolated to $m = 0$ when $\gamma = 1$ and $\log_{10} \gamma = 0$, so $E^\circ = (E + 0.1182 \log_{10} m)_0$, i.e. the intercept on the axis obtained by extrapolation. Having obtained this the equation contains only one unknown and may be solved at all concentrations. As a general method it should be borne in mind that this is only practicable when the salt corresponding to the silver chloride is very sparingly soluble, since otherwise, in the all-important very dilute solutions, the concentration of the salt is comparable with that of the acid and the activity is accordingly modified.

An important convention in the treatment of electromotive force has its echo in tabulating molecular free energies, and therefore requires consideration here. In such a cell as



for which the reaction is



the total electromotive force, E° , representing the tendency for positive electricity to pass from left to right through the cell as written and for the reaction to take place as expressed by reading the equation from left to right, is regarded as the sum of the two individual electrode potentials, $E_{\text{H}_2, \text{H}}$ and $E_{\text{Cl}', \text{AgCl}, \text{Ag}}$, which measure, respectively, the driving force of the reactions $\frac{1}{2}\text{H}_2 = \text{H}^+ + e$, and $\text{AgCl} + e = \text{Ag} + \text{Cl}'$, where the same conventions as to sign are observed and e denotes an electron

passing to or from the connecting wire from or to the electrode according to whether it appears on the right or left of the equation. We do not know either of these values separately, but if *one* is assumed the other is thereby determined. It is usual to assume $E^\circ_{\text{H}_2, \text{H}^+} = 0$ whence $E^\circ_{\text{Cl}', \text{AgCl}, \text{Ag}} = E^\circ$ of the above cell, which may be taken as 0.2258 when the chloride has been prepared by electrolysis. It is also possible to determine the values of E° for other single electrodes by comparison with these. For example, from the cell $\text{Zn(s)}, \text{ZnCl}_2\text{aq.}, \text{AgCl}, \text{Ag}$ studied by Horsch,²⁸ assuming the activity coefficient of the salt to be the same as that for barium chloride, Lewis³ calculates $E^\circ = 0.9839 = E^\circ_{\text{Zn}, \text{Zn}^{++}} + E^\circ_{\text{Cl}', \text{AgCl}, \text{Ag}}$, whence $E^\circ_{\text{Zn}, \text{Zn}^{++}} = 0.7581$. In a manner similar to that employed for the silver chloride electrode it has been calculated that $E^\circ_{\text{Cl}', \text{HgCl}, \text{Hg}} = 0.270$, while Lewis and Rupert²⁹ found for the cell $\text{Cl}_2, \text{HCl aq.}, \text{HgCl}, \text{Hg}$ the value $E^\circ = -1.0894$, whence $E^\circ_{\text{Cl}_2, \text{Cl}'} = -1.3594$ and so on.

In combining these equations it is important to keep a constant convention as to sign. It is convenient to make positive values of electromotive force represent the tendency for positive electricity to pass from left to right through the cell as written and to write the chemical equation in such a way that reading from left to right expresses the reaction which occurs when this takes place. This is in harmony with the previous convention as to ΔF and the equation $\Delta F = -nEf$ joules. Single electrodes and their reactions are treated the same way so that

$$E^\circ_{\text{Cl}_2, \text{Cl}'} = -1.3594$$

indicates that there is a negative tendency for positive electricity to pass from left to right across the electrode Cl_2, Cl' and for the reaction $\text{Cl}' + e = \frac{1}{2}\text{Cl}_2$ to occur, whilst

$$E^\circ_{\text{Cl}', \text{Cl}_2} = +1.3594$$

indicates that there is a positive tendency for positive electricity to pass from left to right across the electrode Cl', Cl_2 and for the reaction, $\frac{1}{2}\text{Cl}_2 = \text{Cl}' + e$ to take place. Both show equally that there is a tendency towards ionisation when chlorine gas and chloride ions, each at their conventional unit activity, are brought together.

It is not suggested that these single electrode potentials are correct but, from the manner of their derivation, it is clear that

if there is an error in the assumed value of $E^\circ_{\text{H}_2, \text{H}^+}$, all cationic electrode values will be in error by the same amount and in the same direction (i.e. too high or too low), while all anionic electrode values will be in error by the same amount but in the opposite direction. Since all cells may be reduced to the sum of unlike, or the difference of like, electrodes, these errors must necessarily cancel. Values for the free energy change of formation of individual ions at unit activity from the given electrodes are determined from these values by the equation $\Delta F^\circ = -nfE^\circ$. These also are individually in error, being based on the arbitrary assumption that for the reaction,

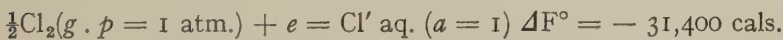


but in the same way as above, the errors must cancel in any practical combination. Consequently, such statements as

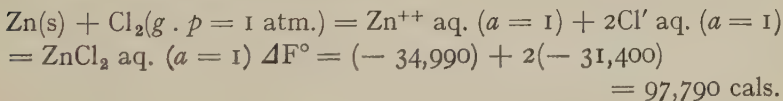
$$\begin{aligned}\text{Zn} &= \text{Zn}^{++} + 2e, \Delta F^\circ = -2 \times 96500 \times 0.7581 \\ &= -146300 \text{ joules} = -34,990 \text{ cal.}\end{aligned}$$

are convenient in tables of molecular free energies because they can be used in combination with other such terms with accuracy, but they do not pretend to represent the truth in themselves.

For example, from the above value of $E^\circ_{\text{Cl}', \text{Cl}_2}$ is found for the reaction

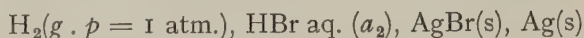


and combining this with the value for the formation of zinc ions



From this is obtained the partial molecular free energy of formation from its elements of zinc chloride in aqueous solution at any concentration for which the activity is known. In particular, if the concentration and activity coefficient of the saturated solution is known (which is not the case as regards the activity coefficient in this example) the chemical affinity of the formation of the solid salt from its elements may be calculated, since the partial molecular free energy of the salt in saturated solution is the same as the molecular free energy of the pure solid salt (*vide* Ex. 18, Chap. VI.).

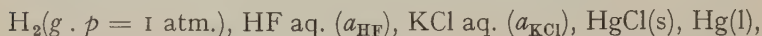
The fullest use of such a method of treatment would require a knowledge of the individual activities of the separate ions which is as yet lacking. The question has not arisen so far because only cells with a single electrolyte have been considered. Thus, in the cell



treated as a whole, $E = E^\circ - 0.0591 \log a_2$ at 25°C. , whilst if it be represented as divided into the sum of the two electrode potentials we write,

$$\begin{aligned} E &= E^\circ_{\text{H}_2, \text{H}^+} - 0.0591 \log a_{\text{H}^+} + E^\circ_{\text{Br}^-, \text{AgBr}, \text{Ag}} - 0.0591 \log a_{\text{Br}^-} \\ &= E^\circ_{\text{H}_2, \text{H}^+} + E^\circ_{\text{Br}^-, \text{AgBr}, \text{Ag}} - 0.0591 \log (a_{\text{H}^+} \times a_{\text{Br}^-}) \end{aligned}$$

and $(a_{\text{H}^+} \times a_{\text{Br}^-}) = a_2$ which we know. But in the case of a cell where there is more than one electrolyte, such as

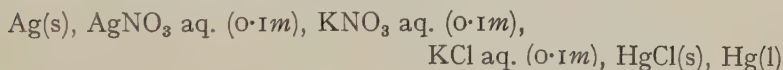


there are two difficulties. The first is, are we justified in assuming that the electromotive force is represented by the sum of the effects at the two electrodes only or will there be some further effect at the liquid junction? Since the total electromotive force varies slightly with the manner of making the liquid junction this question must be answered in the sense that some such effect does arise but is relatively small. Experience and, to some extent, theory suggest that if a saturated solution of potassium chloride be interposed between the two liquids, forming a bridge between them, the liquid junction electromotive force is reduced to negligible proportions and in other cases where the junction occurs between solutions having a common ion various formulæ have been proposed which would seem more or less satisfactorily to express the probable value, whence the effect due to the electrodes alone may be calculated from the total measured value. Assuming then that this difficulty is disposed of and that the sum of the electrode effects is known, this would be written,

$$E = E^\circ_{\text{H}_2, \text{H}^+} - 0.0591 \log a_{\text{H}^+} + E^\circ_{\text{Cl}^-, \text{HgCl}, \text{Hg}} - 0.0591 \log a_{\text{Cl}^-},$$

but since the two ions are no longer present in the same solution it is no longer the case that we know the product of their activities. We may know (e.g. from freezing-point measurements) a_{HF} and a_{KCl} but without some further assumption this does not

tell us the values of a_{H^+} and a_{Cl^-} . Formerly, when the activities were supposed to be equal to the concentrations of the ions as such, it was assumed that $a_{\text{H}^+} = a_{\text{F}^-}$, each therefore being equal to $a^{\frac{1}{2}}_{\text{HF}}$ whilst, in a similar manner, $a_{\text{Cl}^-} = a^{\frac{1}{2}}_{\text{KCl}}$ and calculations were made on that postulate. More recent work has shown, however, that it is probably unsound. An interesting theorem has been put forward by G. N. Lewis³ under the name of "the principle of ionic strength" by which these independent activities may be calculated, but there is no space to enter into this here. In any case it is admittedly a law which is only approached as the solution becomes more and more dilute and the concentrations at which it fails sufficiently to introduce serious error have not yet been determined. Nevertheless, it has been employed in the determination of the single electrode potentials for several elements where the only data available were derived from cells containing more than one electrolyte, e.g. silver, from electromotive force measurements of the cell,



for which Lewis gives, $E^\circ_{\text{Ag}, \text{Ag}^+} = -0.7995$. Such values, although probably very close to the truth, are less reliable than those discussed hitherto since they depend upon slightly doubtful formulæ for the correction for the liquid junction potentials and for the determination of the activities of the ions concerned. The same qualification necessarily applies to the values given for the free energy of formation of the individual ions found from the equation $\Delta F^\circ = -nE^\circ f$.

SUMMARY.—The conclusions of this chapter may be summarised as follows: The chemical affinity of reactions involving solutions is affected by the concentration because the (partial) molecular free energy of substances in solution at constant temperature and pressure varies with concentration, usually in a manner which is specific to each solution. It is convenient to express this variation by the introduction of a new term, activity, defined in such a way that the change of (partial) molecular free energy with concentration (only) is proportional to the absolute temperature and to the logarithm of the ratio of the activities, the factor of proportionality being the gas constant,

$$[\Delta \bar{F} = RT \log_e (a'/a)]_{T, x, \text{const.}}$$

To obtain numerical values of activity it is necessary to fix arbitrarily some *one* value in a basic reference state, or the mathematical equivalent of this. Since it is found that, with a suitable choice of molecular weight, the change in activity of each molecular species present as solute approaches proportionality to the corresponding change in concentration (or molarity) as the solution becomes more and more dilute, it is convenient to set arbitrarily $[a = m]_{\text{lim. } m=0}$ and make use of some extrapolation formula, implicitly involving activity, to fix the numerical value in some very dilute solution.

Methods of calculating the ratio of the activities of a solute at two different concentrations from measurements of vapour pressure, freezing-point, and electromotive force have been given : they depend fundamentally upon measuring the free energy changes when different concentrations are employed.

Substances which dissociate in solution, such as electrolytes, require special treatment in the choice of the basic reference state corresponding to the selection of a suitable molecular weight. This is required only for the purpose of the convention that $[a = m]_{\text{lim. } m=0}$ *for the molecular species present at infinite dilution.*

The law of mass action, expressed in terms of activities instead of concentrations, follows from the two laws of thermodynamics and consequently the ratio of activity to concentration is required for the calculation of free energy changes from measured equilibria.

CHAPTER V.

THE NERNST HEAT THEOREM AND THIRD LAW ON THERMODYNAMICS.

IN all that has been considered so far it has been possible to measure chemical affinity only when at least one equilibrium determination had been made (including the artificial equilibrium obtained by exactly counterbalancing the tendency to react of a galvanic cell). But by far the greater number of chemical reactions do not give rise to measurable equilibria, and so it is a matter of great interest to escape from this necessity. A means was found by Nernst in 1906³⁰ as the result of a study of the electromotive force of galvanic cells at low temperature, which revealed the fact that the temperature coefficient of the electromotive force continuously diminished as the temperature was lowered and obviously approached the limit 0. He put forward the law, known after him as "the Nernst heat theorem, that * $[d(\Delta F)/dT]_{p, \text{const.}}$ continuously approaches the limiting value 0 as the temperature is reduced, for all reactions between solids and liquids. Gases of course do not exist at the absolute zero of temperature, and so there is no experimental justification for including them within the scope of the law. In the consequences of this postulate lies the solution of the problem before us.

Nernst argued that, so long as a substance does not change phase or undergo chemical reaction, its heat capacity is a continuous function of temperature which could be represented by a formula of the type, $C_p = a' + b'T + c'T^2 + \dots$ and, as explained in Chapter III., this leads to the equation,

$$\Delta F = \Delta H_0 - a \log_e T \cdot T - \frac{1}{2}bT^2 - \frac{1}{6}cT^3 - \dots + IT \quad (7B)$$

whence

$$d(\Delta F)/dT = I - a \log_e T - bT - \frac{1}{2}cT^2 - \dots \quad (7C)$$

* Nernst's notation is different, but his ideas are quite accurately expressed in these terms.

This is compatible with Nernst's theorem only if

$$I = 0 \quad . \quad . \quad . \quad . \quad (12)$$

and

$$a = 0 \quad . \quad . \quad . \quad . \quad (12A)$$

That is, if the integration constant is zero (for reactions between solids and liquids only), and if the a' term of the heat capacity equations for all such substances depends only upon the number of atoms (which does not change as the result of reaction) and not at all upon the way in which they are arranged to form molecules. At that time but few data on heat capacity at low temperature were available, and Nernst was led to conclude that the molecular heat capacities of all solids and liquids might be represented by formulæ of the type,

$$C_p = 1.5m + b'T + \dots \quad . \quad . \quad (13)$$

where m is the number of atoms in the molecule, so that only b' and the coefficients of any higher powers of T that might be included were specific. Later work, largely by Nernst himself, has shown that such formulæ are inadequate to express the facts, but they serve in many cases for approximate calculation when more precise data are lacking. Thus, assuming the correctness of the heat theorem and the adequacy of equation (13),

$$\Delta C_T = bT \text{ and, from (7A), } \Delta H_T = \Delta H_0 + \frac{1}{2}bT^2,$$

whilst from (7B), $\Delta F_T = \Delta H_0 - \frac{1}{2}bT^2$, whence

$$\Delta F_T = \Delta H_T - \Delta C_T \cdot T \quad . \quad . \quad . \quad (14)$$

A simple example of the application of this is the calculation of the heat of fusion from the melting-point and the heat capacities of the liquid and solid forms at the melting-point. Thus Tamman³¹ gives for the molecular heat capacities of liquid and solid naphthalene, respectively, 0.442 and 0.332 at the melting-point 353° K. Formula (14) then gives 38.8 as the molecular heat of fusion against the experimental value 34.7 cal. For this special case (fusion) Tamman had put forward this equation as an empirical law.

An indirect application to gases along the same lines is also too useful as an approximate guide to be ignored here, although the exposition is a little lengthy. Nernst virtually assumes that the molecular heat capacity of all gases can be represented by an equation of the type $C_p = (3.5 + 1.5m) + b'T$ (13A), whence,

by applying equation (7B) to the reaction liquid (or solid) = vapour ($p = 1$ atm.), using equations (13) and (13A) but not (12) and (12A)

$$\Delta F = RT \log_e p = \lambda_0 - 3.5T \cdot \log_e T - \frac{1}{2}bT^2 - \dots + iT \quad (15)$$

where p is the vapour pressure and λ_0 the latent heat of evaporation calculated for 0° K. from the thermal data as usual (employing Nernst's assumptions as to the heat capacities), or

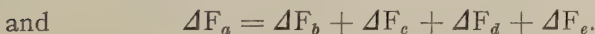
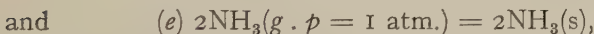
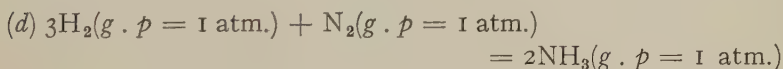
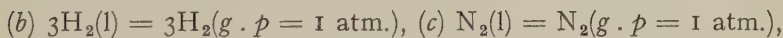
$$\log_{10} p = -\lambda_0/4.576T + 1.75 \log_{10} T + bT/9.152 + \dots + C \quad (15A)$$

where $C = -i/2.303R$. From the vapour pressure curve it is possible to select suitable values of the three constants, λ_0 , b , and C . (Incidentally, after he had done this for several gases he discovered an empirical relationship, between C and Trouton's "constant," which he employed for other gases.)

The application of this to gaseous reactions may perhaps best be illustrated by an example, say, the formation of ammonia. If we imagine the reaction, (a) $3H_2 + N_2 = 2NH_3$, to take place at so low a temperature that all the substances concerned are liquid or solid, by equation (7B)

$$\Delta F_a = \Delta H_0 - aT \cdot \log_e T - \frac{1}{2}bT^2 - \dots + I.$$

But, formally, the same reaction would be effected by the following series of reactions carried out at the same temperature and, though this could not actually be done, the corresponding values for ΔF could be calculated from the vapour pressure and equilibrium pressure data,



Applying equation (7B) to reaction (d) with Greek letters or strokes to avoid confusion, $\Delta F_d = \Delta H' - \alpha T \log_e T - \frac{1}{2}\beta T^2 - \dots + I'$ and equation (15) to ΔF_b , ΔF_c and ΔF_d (multiplied by 3 for the hydrogen, since 3 gram-molecules are concerned, and -2 for the ammonia, since two gram-molecules are *condensed*), summing term by term and equating to ΔF_a , we note that,

$$a = \alpha + 3.5(4 - 2) \text{ and } I = I' + (3i_{H_2} + i_{N_2} - 2i_{NH_3}).$$

But reaction (a) involved only liquids and solids and is therefore subject to the heat theorem, so $I = 0$ and $a = 0$, therefore

$$\alpha = 3.5(2 - 4) \text{ and } I' = 2i_{\text{NH}_3} - 3i_{\text{H}_2} - i_{\text{N}_2},$$

that is, the first constant is determined solely by the change in the number of molecules consequent upon the reaction and the second by a series of individual constants for the gases concerned which may be determined from the separate vapour pressures of the substances. Since $\Delta F_d = RT \log_e k_d$ we may write, as the most general form (cf. 15A),

$$\log_{10} K = -\Delta H_0'/4.576T + 1.75\Sigma n \cdot \log_{10} T + \beta T/9.152 + \dots + \Sigma(nC) \quad (15B)$$

where Σn denotes the change in the total number of molecules consequent upon the reaction and $\Sigma(nC)$ is given by the sum of the values of C for the substances on the left-hand side of the equation, each multiplied by the coefficient appearing in the equation, subtracted from the corresponding sum for the right-hand side. For this reason Nernst calls the C terms the "conventional chemical constants" of the substances to which they refer, "conventional" because they are derived from conventional heat capacity data which are not strictly accurate, and "chemical constants" because, by their aid, the integration constant of any gaseous reaction may be determined in the manner shown. He has given the following table:—

Conventional Chemical Constants ^{30b}							
H ₂	1.6	Cl ₂	3.1	N ₂ O	3.3	NH ₃	3.3
CH ₄	2.5	I ₂	3.9	H ₂ S	3.0	H ₂ O	3.6
N ₂	2.6	HCl	3.0	SO ₂	3.3	CCl ₄	3.1
O ₂	2.8	HI	3.4	CO ₂	3.2	CHCl ₃	3.2
CO	3.5	NO	3.5	CS ₂	3.1	C ₆ H ₆	3.0

The numerical calculation may be illustrated also with reference to the formation of ammonia, using equation (15B) without the b term. Here $\Sigma n = -2$ and $\Delta C_p = -7T$, so $\Delta H' = \Delta H_0' - 7T$. For the heat of formation (heat evolved) of gaseous ammonia Tamaru ³² gives, per gram-molecule, 12,670 cal. at 466° C., 12,700 cal. at 503° C., and 12,900 cal. at 554° C., which, from the above formula, gives for the reaction (2 gram-

molecules formed) $\Delta H_0' = -20,167$, $-19,968$, and $-20,011$ cals., respectively, mean $-20,000$ cals. From the table,

$$\Sigma(nC) = (2 \times 3.3) - (3 \times 1.6) - 2.6 = -0.8.$$

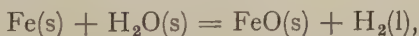
Thus, for this reaction, equation (15B) takes the numerical form,

$$\log_{10} K = + (20,000/4.576T) - 3.5 \log_{10} T - 0.8.$$

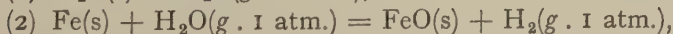
At 400°C. (673°K.) this gives $\log_{10} K = 5.8$, whereas the experimental value interpolated from Haber's ⁵ data is $\log_{10} K = 4.4$ at this temperature. The value $\log_{10} K = 5.8$ is reached at about 450°C. according to the experimental figures. When it is remembered that the sole experimental datum required (apart from that necessary to establish the individual chemical constants) was a measurement of the heat of reaction, which gives an equilibrium distribution within fifty degrees of where it actually occurs, it is evident that this approximate method might be invaluable in planning a research.

This particular case is by no means unduly favourable, but it may be noticed from the general similarity of the chemical constants, that the equation owes more to a wise choice of a generally suitable expression for the specific heats of gases than to the constants themselves whenever there is a change in the number of molecules as a result of the reaction. It is just in those cases where there is no such change that the equation usually leads to the worst results.

Equation (15B) is directly applicable to heterogeneous reactions when it is remembered that the chemical constants for all substances in the liquid and solid states are null, and that such substances do not contribute to the coefficient of the $\log_{10} T$ term, since the b' term of their heat capacity equation, $1.5m$, reappears in the corresponding term for gases, $3.5 + 1.5m$, and therefore cancels in determining ΔC_p . The student should verify this by equating ΔF for the reaction,



to the sum of the ΔF terms for the equivalent series of reactions,



in exactly the same way as has been shown for the formation of ammonia.

It was evident that thermal data at extremely low temperature were required to test the theory and provide accurate figures for the equations. Nernst and others undertook the experimental work and developed a wonderful technique. The results were surprising, since for all substances investigated it was found that, at very low temperature, the heat capacity began to decrease as the temperature was lowered with a suddenness of which there was no indication in the ordinary region. The following figures, for diamond, zinc, and benzene are taken from the work of Nernst³³ and Nernst and Lindemann:—³⁴

Diamond.								
T .	1169	413	358	331	306	284	262	232
C _p .	5.45	2.66	2.12	1.84	1.58	1.35	1.14	0.86
T .	220	209	205	92	88	42	30	—
C _p .	0.72	0.66	0.62	0.03	0.03	0.00	0.00	—
Zinc.								
T .	274	207	94	89	85	80	75	68
C _p .	5.90	5.83	4.55	4.39	4.24	4.17	3.95	3.59
T .	64	61.8	43.7	36.3	34.3	33.1	—	—
C _p .	3.51	3.25	2.17	1.71	1.32	1.25	—	—
Benzene.								
T .	200.9	197.7	80.7	53.45	46.75	40.85	36.1	—
C _p .	1.728	1.678	0.95	0.694	0.611	0.578	0.520	—
T .	34.3	31.1	27.8	24.4	—	—	—	—
C _p .	0.451	0.386	0.348	0.224	—	—	—	—

Fig. 5 shows the plot of C_p against T for zinc and also the curve for C_p/T which we shall require later. This curious behaviour was almost immediately explained by the quantum theory which itself originated from quite a different source, namely, the theory of radiation, according to which a vibrating body (e.g. an atom in a solid) cannot vary its energy continuously but must change, if it changes at all, in steps or "quanta," the quantum in each case being equal to the frequency of vibration multiplied by a universal constant, h , "Planck's constant." When there is plenty to go round, the law of equipartition of thermal energy, on which classical theory rested, can be satisfied within the limits of experimental error, but when there is only a little energy available, the law of quanta makes this impossible. An analogy is offered by the conception of a distribution of money between a number of men, women, and children when it is desired to give

each individual an equal share (law of equipartition), but men must be given a whole number of pounds, women a whole number of shillings, and children a whole number of pence (law of quanta). So long as there is sufficient to give every one a large sum it is possible to satisfy both conditions fairly well, but when there is less than a pound per head some men at least will have to be without anything, since they cannot have less than a whole

C_p and $(C_p/T) \times 10^2$ for Zinc.

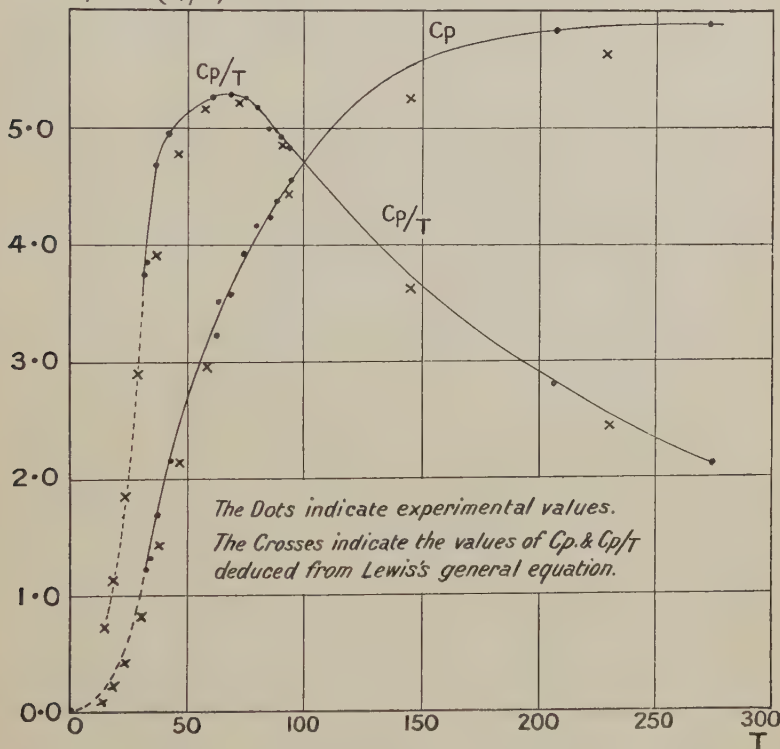


FIG. 5.

pound, and the smaller the total amount the more irregular must the distribution be. Similarly, if the average kinetic energy of the molecules of a perfect monatomic gas at 50° K. (as defined in Chapter I.) is less than the quantum for a carbon atom in diamond, only rarely will the bombardment of the gas molecules supply a carbon atom with sufficient energy for a quantum and, since it cannot take up less, there will be no perceptible thermal energy in the diamond. The same will be true at lower temperatures,

and hence the heat capacity of the diamond at these low temperatures, i.e. the difference in thermal energy at two temperatures one degree apart, will be null. Substances containing atoms vibrating with a lower frequency have a smaller quantum and consequently their heat capacity does not vanish until a lower temperature is reached. Many attempts have been made to deduce the variation of atomic or molecular heat capacities of solids at low temperatures from kinetic theory supplemented by the quantum hypothesis, apparently the most successful being due to Debye,³⁵ which has been fully substantiated in the case of copper at least. We need not follow the details here but must note that, according to Debye, the heat capacity of all solids becomes proportional to the cube of the absolute temperature when this is very low. (The total thermal energy is therefore proportional to the fourth power of the absolute temperature.)

The heat capacities of gases also show some curious anomalies at low temperatures, notably polyatomic gases (e.g. hydrogen at 60° K.)³⁶ lose their power of containing energy of rotation and have the thermal energy content and heat capacity of monatomic gases. This also is accounted for by the quantum theory.

The translational movement may be regarded as a vibration with zero frequency so that the quantum is 0 and the energy content may be varied continuously as postulated by classical theory. Even this may require modification at very low temperatures on account of the influence of collisions, but this complication need not concern us here.

Thus experiment and modern theory combine in supporting one deduction of the Nernst heat theorem, that for solids ΔC_p vanishes at the absolute zero, because C_p itself vanishes. The power equations so far employed are, however, quite inadequate to express the variation of the heat capacity with temperature, especially in the low temperature region where the quantum effect is producing very rapid changes. Given suitable equations and figures it would be, of course, possible to proceed along lines similar to those discussed and obtain "true" chemical constants for the various gases, but such equations are complicated and the numerical values of the constants would be highly specific, so that nearly all the advantage of the approximate equations would be lost, as far as the application to chemical affinity determinations goes.

If full play is to be given to the specific nature of the heat capacity equations of substances a more convenient method for our purpose is available in the use of entropy. Hitherto we have treated entropy as a function which, like free energy, is incapable of expression in absolute terms. We are free, however, to assign the arbitrary value 0 to the molecular entropies of all elements in some specified crystalline form at the absolute zero of temperature. Transition to some other crystalline form, or reaction to form some crystalline compound, at 0° K. would, in general, produce a change in the free and total energies, ΔF_0 and ΔH_0 . But by equation (6) and Nernst's heat theorem,

$$(d(\Delta F)/dT)_{T=0} = -\Delta S_0 = 0,$$

that is, there is no change in entropy, so that the entropy of all crystalline solids at the absolute zero would be zero. Planck states this as a third law of thermodynamics and leaves the applicability of the heat theorem to liquids as an open question.

The entropy of substances at finite temperature is then readily calculable from the thermal data. If, over a given range of temperature, a substance does not change state or undergo chemical reaction, the addition of an infinitesimal amount of heat produces an infinitesimal rise in temperature. If the process is conducted reversibly the heat added is equal to TdS and it is also equal to $C \cdot dT$. The entropy change is the same whether the process is conducted reversibly or not, and consequently $T \cdot dS = C \cdot dT$. Thus, when heated over a finite range of temperature,

$$\Delta S = \int_{T_1}^{T_2} C \cdot dT/T = \int_{T_1}^{T_2} C \cdot d \log_e T \quad . \quad . \quad (16)$$

Equation (16) can be applied to substances which preserve their chemical and physical state from zero temperature upwards, to

T say, and the integration of $\int_0^{T_2} C \cdot dT/T$ may be performed

graphically by plotting C/T against T , as has been done for zinc in Fig. 5. It will be noticed that experimentally, not only C but also C/T appears to approach 0 as the temperature is indefinitely lowered, and Debye's formula, according to which C/T is proportional to the square of the temperature at very low temperature, supports this, so that the integral is finite and can

be evaluated. Thus, by means of the third law and the thermal data the entropy of zinc at ordinary temperature may be determined.

When a change of state (e.g. melting) takes place at some temperature it is possible to add a finite quantity of heat without increasing the temperature at all. If this change occurs at the equilibrium temperature (e.g. the melting-point) there is no change in the free energy content and from equation (3),

$$(\Delta F = 0 = \Delta H - T \cdot \Delta S)_{T = \text{melting-point.}}$$

Hence the entropy change is calculated from the total energy change of the process (here a fusion) divided by the temperature at which it takes place (here the melting-point). The entropy change of the new phase as the temperature is increased may then be determined by graphical integration of equation (16) between the limits T_m and T' , the desired higher temperature. In this way the entropy of substances in states which they cannot assume at low temperature may be determined. In illustration we may quote the determination of the molecular entropy of liquid bromine at 25°C. by Latimer and Hoenshel.³⁷ They determined the heat capacity of solid bromine from the triple point of hydrogen, 14°K. , to the melting-point and plotted their results against $\log_{10} T$. Also, for the lower measurements, they plotted $\log C_p$ against $\log T$ and found the plot to be linear so that it may be represented by the formula

$$\log_{10} C_p = b \log_{10} T + \log a,$$

where b is given by the slope and $\log_{10} a$ by the intercept on the axis $\log_{10} T = 0$. Consequently, at low temperature, their results justified the relation $C_p = aT^b$, where the constants a and b are known. Assuming that this relation holds down to the absolute zero of temperature, $C_p \cdot dT/T$ can therefore be integrated between the limits 0 and some low temperature in the region where the formula applies. They chose 15.85°K. as the upper limit when the integral is 0.510. They considered, however, that the extrapolation was probably not entirely justifiable, as Debye's law ought to be approached at still lower temperatures, and estimated that the true value of the integral, if the results at very low temperatures had been known, would be 0.45. Since, by Planck's law, the entropy of solid bromine at 0°K. is

0, this should be the value at $15\cdot85^\circ$ K. The area under the graph of C_p against $\log_{10} T$ from this point up to the melting-point, $265\cdot9^\circ$ K., gives the increase in entropy on heating from the first to the second temperature, and was determined graphically as 12.15. The increase in entropy resulting from fusion at the melting-point was calculated from Regnault's³⁸ determination of the heat of fusion, 1290 cal., which, divided by the temperature, gives 4.85. Finally, assuming Regnault's value for the heat capacity of liquid bromine, 8.4, as constant over the temperature range from the melting-point to 298° K., the increase in entropy consequent upon liquid bromine being heated from the former to the latter temperature is

$$8\cdot4(\log_e 298 - \log_e 256\cdot9) = 0\cdot95.$$

Thus, the total entropy of liquid bromine at 25° C. is

$$S_{298} = 0\cdot45 + 12\cdot15 + 4\cdot85 + 0\cdot95 = 18\cdot40$$

entropy units (cals. per degree). All these figures are for 80 grams (in round numbers) of bromine, the gram-atom; for the gram-molecule, assuming a molecule to contain two atoms, these figures must be doubled. The same authors determined the entropy of lead bromide in a similar manner, except that there is here no complication of a change of phase, and that of lead is known from the work of Nernst.³³

For a reaction at constant temperature we have, from equation (3), $[\Delta F = \Delta H - T \cdot \Delta S]_{T, \text{const.}}$ and since ΔS may be determined from the individual entropies, and ΔH from a calorimetric heat of reaction or from the individual heats of formation, ΔF may be determined from thermal data only without the necessity for an equilibrium measurement. For the reaction, $\text{Pb(s)} + \text{Br}_2(\text{l}) = \text{PbBr}_2(\text{s})$ at 25° C.,

$$\Delta S = S_{\text{PbBr}_2} - S_{\text{Pb}} - S_{\text{Br}_2} = 39\cdot75 - 36\cdot80 - 15\cdot53 = -12\cdot58.$$

For ΔH we have the value $-66,350$ cal. by Braune and Koref,³⁹ and $-65,580$ cal. from the work of Krahmer⁴⁰ and of Webb,⁴¹ mean $-65,965$ cal., whence,

$$\Delta F = -65,965 + (298 \times 12\cdot58) = -62,215 \text{ cal.}$$

In this case we have the check of an experimental value from the electromotive force measurements of Gerke,⁴² $-62,000$ cal. The value of this method to organic chemistry can hardly be

over-estimated, since it is of practically universal applicability. Here, too, it is almost always possible to determine the heat of formation of the substances concerned from their heats of combustion. It must be admitted, however, that calorimetric measurements of heats of reaction are usually by no means highly accurate, although Richards ⁴³ has succeeded in refining the technique so highly that it would be possible to make such measurements as accurately as any others in the domain of physical chemistry. Another drawback is the necessity for determining heat capacities at very low temperatures indeed, and facilities for these measurements are not to be had in every laboratory. On the basis of the equations of Debye and Einstein, G. N. Lewis ³ has shown that the plot of C_v^* against $\log_{10} T - \log_{10} \theta$ is the same for all isotropic solids, θ alone being a characteristic constant so that, theoretically, a single heat capacity determination fixes the whole course of the curve, and consequently establishes the value of θ (in practice, of course, as many points as possible will be measured, but they need not be at very low temperature), and having integrated $C_v \cdot d \log_e T$ for one such substance the value for any other, for which θ is known, is readily calculated. The relation between C_p and C_v follows fairly simple laws in most cases, making it possible to calculate the desired integral of $C_p \cdot d \log_e T$ from the known values (at different temperatures) of the one fundamental curve. The calculated values of C_v and C_v/T for zinc are shown as crosses in Fig. 5. More complicated crystals were found in many cases to conform to a somewhat similar curve on the assumption that C_v was always the same function of $n(\log_{10} T - \log_{10} \theta)$, where two characteristic constants are involved. Parks ⁴⁴ and his co-workers have determined the heat capacities of many organic substances down to the temperature of liquid air, and have used this formula to extrapolate their results down to the absolute zero, determining the constants from their own lowest measurements. It is stated, however, that they regard this method as rather a rough approximation, and consider that the entropies so calculated at 90° K. may be in error by 10 or 20 per cent. For the increase in entropy above this temperature, of course, they have experimental values. Unfortunately, the

* C_v is the molecular heat capacity at constant volume.

entropy at 90° K. is a considerable fraction of the total entropy at 25° C., e.g. for butyl alcohol $S_{90} = 12.75$, as determined from the assumed extrapolation formula, and $S_{298} = 47.2$ from the former value and their experimental results (including the entropy change of fusion) at the higher temperatures. Thus the latter value may be as much as 5 per cent. in error. These, however, are temporary difficulties, and as specific heat measurements are pushed to lower and lower temperatures and calorimetric measurements are improved, data will become available from which the free energy of formation of organic substances may be determined with considerable accuracy, and the chemist attempting a new synthesis will be able to calculate in advance whether the proposed process is thermodynamically possible or not. If the former it might possibly, but not certainly, succeed, if the latter it is impossible, and time and effort can be saved for a more useful purpose.

The entropy at the absolute zero of substances other than crystalline solids is a subject of much theoretical interest and still under debate. For the practical purpose of applying the doctrines of chemical affinity, however, the subject is almost immaterial since the whole discussion turns on abnormalities in the heat capacities which might be found at inaccessibly low temperatures. The statement of the third law by Lewis and Gibson,⁴⁵ "If the entropy of each element in some crystalline state be taken as zero at the absolute zero of temperature, every substance has a finite positive entropy, but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances," is practically undisputed, and suffices for practical needs. From this it follows that, for any chemical reaction, ΔS is finite or null at all temperatures, even at the absolute zero. Then, since

$$\Delta F = \Delta H - T \cdot \Delta S,$$

it follows that $\Delta F_0 = \Delta H_0$, since ΔS is not infinite when $T = 0$.

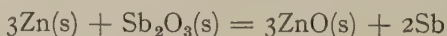
CHAPTER VI.

APPLICATIONS.

THE primary use of the theorems and equations which have been developed is to enable us to calculate from existing data what the possibilities of reaction may be in some new case. The accuracy with which this can be done depends upon the completeness and accuracy of the available data, and it is no small part of a skilful use of the subject to be able to supply deficiencies by means of approximate rules or deductions based on analogy which, though they cannot be expected to give perfectly accurate results, may prove of invaluable assistance in planning a research. The examples here to be given have been selected rather with the purpose of emphasising this point of view than for demonstrating how accurately the more elaborate equations can represent the facts in well-known cases where the data are exceptionally complete. At the same time, they may be made to serve as a recapitulation of the principles which have been expounded in the foregoing chapters.

The starting-point is usually the table of molecular free energies of formation of substances in conventional "standard" states at 25° C., and the simplest case of all is one in which it is required to determine whether reaction is possible between substances in their standard states at this temperature.

Example 1.—A mixture of finely powdered antimony trioxide and zinc has been made up to demonstrate Marsh's test. Is it really stable? The free energy change of the reaction,



is equal to the sum of those associated with the dissociation of one gram-molecule of antimony trioxide into its elements and the formation of three gram-molecules of zinc oxide from its elements. Therefore, from the tables,

$$\begin{aligned}\Delta F &= 3\Delta F^\circ_{\text{ZnO}} - \Delta F^\circ_{\text{Sb}_2\text{O}_3} = 3(-75,930) - (-190,720) \\ &= -32,070 \text{ cal.}\end{aligned}$$

The chemical affinity ($= -\Delta F$) is therefore positive, and there is a considerable tendency for the reaction to take place. Whether it will become manifest or not in the case of solids at such low temperature, it is not possible to say. The possibility of reaction, however, exists, and if the powder is exceedingly fine it might occur in a long time.

Usually one or more of the substances will not be in its standard state, and it is then necessary to calculate its molecular free energy of formation in the condition under consideration.

Example 2.—Will the mixture in the previous example be stable in air or will the zinc oxidise in time?

The free energy change of a reaction between substances which are not in their "standard" states (ΔF) is connected with that in which they are (ΔF°) by equation (10) which may be written, $\Delta F = \Delta F^\circ + RT \sum (n \log_e a)$. In this case, for the reaction, $\text{Zn(s)} + \frac{1}{2}\text{O}_2\text{(g)} = \text{ZnO(s)}$ we have, from the tables, $\Delta F^\circ = -75,930$, and the activity of the two solids is unity, that is, they are in their "standard" states. The activity of the oxygen is, however, equal to its partial pressure, 0.2 atm. in air, so, on substituting in the various numerical values,

$$\begin{aligned}\Delta F &= -75,930 - (1.9869 \times 298.1 \times \frac{1}{2} \times 2.303 \times \log_{10} 0.2) \\ &= -75,453.\end{aligned}$$

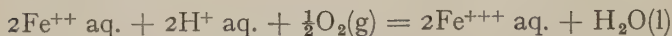
Thus the chemical affinity for the reaction under these conditions is positive and high and, unless the protective power of the zinc oxide coating proves sufficiently high to preserve the interior of the powder granules from contact with the air, it must be expected that the mixture will be ultimately spoilt, if it is left exposed to the air.

In homogeneous solution, since the (partial) molecular free energy of all substances decreases as the concentration is reduced, reaching minus infinity when the concentration is infinitely small, a condition will always be reached in theory for which the sum of the molecular free energies of the reactants is equal to that of the resultants, when there is equilibrium, though in practice it may be that the equilibrium concentrations of some of the substances are imperceptible. Therefore in all cases of homogeneous

equilibrium it is most convenient to calculate the equilibrium constant from the equation $\Delta F^\circ = -2.303RT \log_{10} K$.

Example 3.—What are the conditions of equilibrium between ferrous and ferric ions in aqueous solution saturated with air at 25° C.?

The reaction is



for the anions are unaltered and therefore do not require to be taken into consideration. From the tables,

$$\begin{aligned} \Delta F^\circ &= 2(-3120) + (-56,560) - 2(-20,350) - 2 \times 0 \\ &\quad - \frac{1}{2} \times 0 = -22,100. \end{aligned}$$

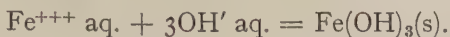
Therefore $\log_{10} K = + (22,100/1364) = 16.20$, and $K = 1.6 \times 10^{16}$. It is really dissolved oxygen which effects the oxidation, but as this is in equilibrium with the gas above (and therefore has the same partial molecular free energy as in the gas), it is convenient to disregard the intervening act of solution, and we may take as the standard state for the oxygen that usually selected when dealing with it as a gas, namely, the pure gas at atmospheric pressure. The activity of oxygen in air is equal to its partial pressure, 0.2 atm., and this will be its activity (with reference to the same standard state) in the saturated solution which is in equilibrium with the air. If the solution is reasonably dilute we may take the activity of the water as unity without serious error, though this is strictly the case only for infinitely dilute solutions. Then $K = a_{\text{Fe}^{+++}}^2 / a_{\text{Fe}^{++}}^2 \times a_{\text{H}^+}^2 \times 0.2$.

Therefore $a_{\text{Fe}^{+++}} / a_{\text{Fe}^{++}} = 5.6 \times 10^7 \times a_{\text{H}^+}$.

What is really desired is the relationship between the concentrations of the two ions, but it is not possible to make any exact general statement as to the relation between activity and concentration. This depends on the total concentration, the nature of the anions and any other ions which may be present, and the determination of the individual activity coefficients would hardly be possible in the present state of our knowledge. However, if the solution be moderately dilute we may expect that the activity coefficients will be not very different, and so the same relation will be approximately true of the concentrations.

The activity of hydrogen ion in neutral solution has been

determined by electromotive force measurements to be of the order 1×10^{-7} ,* so that in neutral solution the ratio of ferric to ferrous ion should be about 5.6. It is, however, probable that no appreciable quantity of ferric iron could exist in neutral solution owing to the reaction



No adequate data are available for determining this equilibrium, but it seems to be of such an order that in neutral solution, where $a_{\text{OH}'} = 1 \times 10^{-7}$, the concentration of ferric iron is negligible. It would be a million times as great in a solution where

$$a_{\text{OH}'} = 1 \times 10^{-9},$$

but then $a_{\text{H}^+} = 1 \times 10^{-5}$ and the ratio of ferric to ferrous ions at equilibrium would be 560. This accounts for the fact that the spontaneous reduction of ferric ion has never been observed.

The difficulty in connecting activity with concentration always limits the usefulness of the free energy tables with reactions in solution except in those special cases, such as gases, very dilute solution, or mixtures of very similar organic liquids where general laws are obeyed more or less closely.

It is often desirable to express chemical affinity in terms of standard states other than those given in the table which merely requires that the free energy change associated with the change from one standard state to the other shall be known or determinable.

Example 4.—Examine the Williamson synthesis of ether.

The reaction may be regarded as essentially



and the free energies of formation of the organic liquids have been determined by means of the third law. From the values given in the tables,

$$\Delta F^\circ = (-33,600) + (-56,560) - 2(-44,000) = -2160.$$

The chemical affinity is positive, but not large, and one can well understand that a catalyst (the sulphuric acid) is required. The simultaneous liberation of ether and water shows that the acid

* See Ex. 16.

acts as a catalyst only and plays no essential part in the energetics of the reaction. (The effect of the increased temperature at which the process is carried out in practice will be considered later.) Quite conceivably some other catalyst, perhaps a heterogeneous one, may be discovered, in which case the reaction might be produced in what is virtually a mixture of the liquids. It is easy to calculate the equilibrium as before, but it would be difficult to connect the activities with concentrations, since the non-miscibility of ether and water warns us of abnormalities. It is, on the other hand, easy to calculate the equilibrium composition which would result if the reaction could be catalysed in the *gaseous* state. Now the free energies of formation from the elements of the substances as given in the tables are those for the pure liquids, and must therefore also be that for the vapours in equilibrium with the liquids, that is, for the gases *at the pressures at which they are in equilibrium with the liquids, the vapour pressures*. If we take the pure liquid as the standard state, then the activity of the liquid and of the vapour in equilibrium with it is unity. But it is more convenient to set the activity of gases equal numerically to their pressure in atmospheres (so long as they may be regarded as obeying the law of perfect gases), which automatically sets a new standard state such that the change from it to the vapour pressure p involves a free energy change $RT \log_e p$. Thus, $\Delta F^\circ_{\text{gas}} = \Delta F^\circ_{\text{liquid}} - RT \log_e p$. It will thus be seen that the calculation is the same as would be involved if the gases could be compressed to atmospheric pressure without departing from the perfect gas law. The fact, however, that this is not physically possible does not in any way invalidate the choice of this molecular free energy as defining the standard state, for it simply serves as a basis of calculation which has the advantage that, for partial pressures at which the substances can exist as gases, the activity is numerically equal to the pressure.

The vapour pressures at 25° C. are 61 mms. for ethyl alcohol,⁴⁶ 525 mms. for ether,⁴⁷ and 23.55 mms.⁴⁸ for water, so that the molecular free energies for the conventional standard state of gases are:—

for alcohol, $\Delta F^\circ_{\text{gas}} = (-44,000) - 1364 \log_{10} (61/760) = -42,500$
 for ether, $\Delta F^\circ_{\text{gas}} = (-33,600) - 1364 \log_{10} (525/760) = -33,380$
 for water, $\Delta F^\circ_{\text{gas}} = (-56,560) - 1364 \log_{10} (23.55/760) = -54,500$

whence

$$\log_{10} K_p = -\Delta F^\circ_{\text{gas}}/1364 = + (2880/1364) = + 2.11$$

or $K = 129$.

Since $K = p_{\text{H}_2\text{O}} \times p_{(\text{C}_2\text{H}_5)_2\text{O}}/p^2_{\text{C}_2\text{H}_5\text{OH}}$ the product of passing pure alcohol vapour over a catalyst which produced equilibrium at 25°C . would contain water vapour and ether at partial pressure 0.479 atm. each, leaving alcohol vapour at a partial pressure of 0.042 atm. , for $0.479^2/0.042^2 = 130$. Thus conversion would be nearly complete.

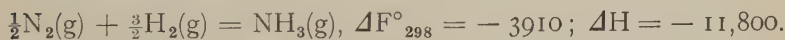
The effect of temperature on an equilibrium constant is obtained from equation (6A), as applied to changes instead of individual substances, $d(\Delta F/T) = -\Delta H \cdot dT/T^2$, from which we have, $d \log_{10} K = + \Delta H \cdot dT/2.303 \times R \times T^2$. The exact integration of this requires a knowledge of the variation of ΔH with temperature, which in turn requires a knowledge of the thermal capacities of the substances concerned which is not usually available. Fortunately, the results of assuming that ΔH does not change above 25°C . usually afford very satisfactory approximations to the actual facts as determined by experimental measurements, and the formula resulting from the definite integral on this assumption may be employed with considerable confidence, namely,

$$\log_{10} K_T = \log_{10} K_{298} + (\Delta H/1364) - (\Delta H/4.576T).$$

(See Ex. 16.)

Example 5.—Calculate the equilibrium constant for the formation of ammonia at 600°C .

From the tables, for the reaction,



Therefore $\log_{10} K_{298} = + (3910/1364) = 2.867$

$$\begin{aligned} \log K_{898} &= \log_{10} K_{298} - (11,800/1364) + (11,800/4.576 \times 898) \\ &= -2.913 = \bar{3}.087. \end{aligned}$$

The experimental value is $\bar{3}.178$.⁵

Example 6.—Calculate the effect of temperature on the Williamson synthesis of ether. (Cf. Ex. 4.)

The heat of reaction in the liquid state may be calculated directly from the values given in the tables, but, for the vapour state, the latent heats of vaporisation are also required. It is

probably more accurate to calculate $\Delta F^\circ_{\text{liquid}}$ first for some temperature other than 25°C. , find from this the value of $\Delta F^\circ_{\text{gas}}$ at this temperature, from vapour pressure data, and combine this result with $\Delta F^\circ_{\text{gas}}$ at 25°C. (already obtained in Ex. 4) to obtain ΔH_{gas} . Thus, for the reaction,



from the tables,

$$\Delta H_{l_{298}} = (-66,000) + (-68,470) - 2(-65,660) = -3150 \text{ cal.}$$

From Example 4, $\Delta F^\circ_{l_{298}} = -2160 \text{ cal.}$

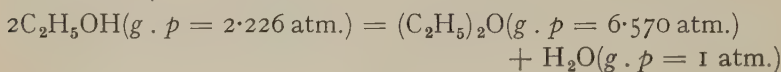
By integration of equation (6B) on the assumption that ΔH is constant, $\Delta F = \Delta H + IT$ and in this case

$$I = (-2160 + 3150)/298 = 3.222.$$

Therefore,

$$\Delta F^\circ_{l_{398}} = -3150 + 3.222 \times 398 = -1828 \text{ cal.}$$

At 100°C. the vapour pressures are 1.000, 2.226,⁴⁷ and 6.570⁴⁷ atm., respectively, for water, ethyl alcohol, and ether. The same value -1828 cal. therefore measures the free energy of the reaction,



and for the free energy of the reaction between the substances all in their conventional standard states for gases, by equation (10),

$$\Delta F^\circ_{g_{398}} = -1828 - \{4.576 \times 398 \times (\log 6.570 + \log_{10} 1 \\ - 2 \log_{10} 2.226)\} \\ = -1828 + (4.576 \times 398 \times 0.4811) = -952 \text{ cal.,}$$

$$\text{and } \log_{10} K_{g_{398}} = +952/4.576 \times 398 = 0.523.$$

Further,

$$\log_{10} K_{g_{398}} = \log_{10} K_{g_{298}} + (\Delta H_g/1364) - (\Delta H_g/4.576 \times 398), \\ \text{so } \Delta H_g = (-1.592 \times 1364 \times 1821)/457 = -8632 \text{ cal.}$$

Accordingly, dealing now with the gaseous reaction and dropping the suffix g ,

$$\log_{10} K_T = 2.120 - (8682/1364) + (8682/4.576T) \\ = -4.244 + 1897/T.$$

The preparation of ether is usually carried out at 140°C. , say 400°K. At this temperature,

$$\log_{10} K = -4.244 + 4.743 = +0.499, \text{ and } K = 3.15.$$

We do not know the relation between concentration and activity in the liquid, but, if equilibrium is attained there, it must be attained in the vapour which distils off. Consequently, this should consist of about one-fifth (molar fraction) alcohol and two-fifths each water and ether, making

$$p_{\text{ether}} \times p_{\text{water}}/p_{\text{alcohol}}^2 = 4,$$

which is as near to the calculated value as the accuracy of the figures permits. As a matter of fact, the accuracy here is not high. The free energies of formation were obtained from the difference of two large terms, ΔH and $T \cdot \Delta S$, the latter of which may be in error by as much as 5 per cent., while the former is itself obtained as the difference of two large terms, the heats of combustion of the constituent elements and of the substance itself. An error of 1364 cal. in ΔF_{298}° (and this amount may be found in the heat of formation alone) makes an error of a unit in $\log_{10} K_{298}$ and a tenfold error in the actual equilibrium constant. Thus the actual equilibrium distribution may be in very considerable error. (It usually works out, however, that the calculated equilibrium distribution is attained within some fifty degrees of the temperature for which it was calculated, and this is a very valuable guide when a reaction is the subject of a new research.) We also learn from the formula that the reaction is adversely affected by increased temperature. At lower temperatures, of course, the preparation is hindered by the appearance of another reaction, the formation of ethylene. There are, however, no available data for estimating the value of the equilibrium constant in this case.

Whilst the more elaborate formula given on page 45 should express the variation of $\log_{10} K$ with temperature better, since it takes account of the variation of ΔH , it is but rarely that the necessary data are available and, more often than not, the difference between the figures as calculated from the two equations is less than the error introduced in the determination of ΔH .

Although reactions involving gases or solutions theoretically always reach an equilibrium state, if the reaction constant be sufficiently large it will not be possible to prove the presence of the reactants analytically. Equilibrium constants, however, are

very sensitive to temperature, and the fact that the value at 25° C. is too great to permit practical demonstration does not preclude the possibility of obtaining a measurable equilibrium at some higher temperature, or even of K becoming so small that it is not possible to prove experimentally the existence of the resultants, i.e. of the reaction proceeding to practical completion in the reverse direction. The possibility of any theoretical equilibrium becoming accessible to measurement is readily calculated from the free energy and total heat changes as follows:—

By equation (10A), $\Delta F_0 = -RT \log_e K$, so $\log_{10} K_{298} = -\Delta F^\circ/1364$.

Again, by equation (6B), $d(\Delta F/T) = -\Delta H \cdot dT/T^2$, and if ΔH be assumed constant, which is very near the truth, by integration between 25° C. (298° K.) and some temperature, T ,

$$(\Delta F/T) - (\Delta F_{298}/298) = (\Delta H/T) - (\Delta H/298),$$

or $\log_{10} K_T = (-\Delta F_{298}/1364) + (\Delta H/1364) - (\Delta H/4.576T)$.

As T becomes infinitely large, the last term becomes negligible,

and $[\log_{10} K = (\Delta H - \Delta F_{298})/1364]_{\lim T, \text{ infinitely large.}}$

Thus if ΔH is of opposite sign to ΔF_{298} $\log_{10} K$ becomes numerically larger as the temperature is increased and the conditions for demonstrating equilibrium analytically become less favourable. If ΔH is of the same sign as ΔF but is numerically less, $\log_{10} K$ will become numerically smaller as the temperature is raised and the conditions for experimentally measuring equilibrium will improve, but, at any temperature, $\log_{10} K$ retains the same sign as at 298, and it is a question of the numbers involved as to whether the equilibrium can be studied practically or not (*vide* Ex. 19). In any case, the reaction cannot be made to go to practical completion in the reverse direction.

If, however, ΔH is of the same sign as ΔF_{298} and is numerically greater, $\log_{10} K$ must change sign at some temperature, and it is certain that demonstrable equilibrium could be attained (as far as numerical values go. In certain cases, often met with in organic chemistry, other difficulties intervene.) A convenient critical value is offered by the case $K = 1$, when $\log_{10} K$ and ΔF are zero. If T' is the corresponding temperature, from the equation given, $(\Delta H - \Delta F_{298})/1364 = \Delta H/4.576T'$ or

$$T' = 298\Delta H/(\Delta H - \Delta F_{298}) = \Delta H/\Delta S.$$

Example 7.—Will the action of hydrogen on silver sulphide give rise to a measurable equilibrium?

The reaction is $2\text{AgS(s)} + \text{H}_2\text{(g)} = \text{H}_2\text{S(g)} + 2\text{Ag(s)}$. From the tables,

$$\Delta F^\circ_{298} = (-7840) - (-2260) = -5580,$$

and $\log_{10} K = 4.09$. Hence at 25°C . the equilibrium composition of the gases would require only one in ten thousand parts of hydrogen. But $\Delta H = (-4760) - (-3330) = -1430$, therefore, as the temperature is increased, $\log_{10} K$ approaches the limit $(-1430 + 5580)/1364 = 3.09$. Thus, even at the highest temperatures the partial pressure of the hydrogen will not exceed one-thousandth that of the hydrogen sulphide. Unless very sensitive analysis is possible the answer must be in the negative.

Example 8.—Will the action of hydrogen on lead sulphide give rise to a measurable equilibrium?

The reaction is $\text{PbS(s)} + \text{H}_2\text{(g)} = \text{Pb(s)} + \text{H}_2\text{S(g)}$, and from the tables $\Delta F^\circ_{298} = (-7840) - (-15,275) = +7435$ and

$$\log_{10} K_{298} = -5.45 = \bar{6}.55,$$

hence at equilibrium at 25°C ., $p_{\text{H}_2\text{S}}/p_{\text{H}_2} = 3.55 \times 10^{-6}$, which is unfavourable.

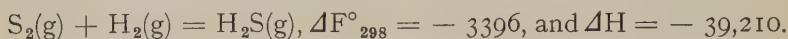
But, $\Delta H = (-4760) - (-18,420) = +13,660$, which is of the same sign as, and numerically greater than, ΔF°_{298} . Consequently, this reaction must be favourable to experiment at some temperature,

$$T' = 298 \times 13,660/6225 = 654.$$

Thus, about 380°C . the partial pressures of the two gases should be equal.

So far as the present author is aware, this equilibrium has not yet been investigated. The calculation suggests that it would serve as a very convenient means for obtaining a check upon the free energy of formation of lead sulphide since the most favourable equilibrium condition for analysis lies at this temperature which is high enough for rapid attainment of equilibrium to be anticipated, and yet well below those temperatures at which the dissociation of hydrogen sulphide is appreciable, especially in the presence of hydrogen. Moreover, the free energies of formation of the other substances concerned are well established.

Example 9.—Discuss the dissociation of hydrogen sulphide. The heat, and free energy, of formation of hydrogen sulphide gas from rhombic sulphur and gaseous hydrogen at 25° C. is given in the tables as, $\Delta H = -4760$ and $\Delta F^\circ_{298} = -7840$. Thus, ΔF° is of the same sign as ΔH and numerically larger, so that no perceptible dissociation into rhombic sulphur and hydrogen is possible at any temperature. On the other hand, for the reaction $2S(s \text{ rhombic}) = S_2(g)$, $\Delta F^\circ_{298} = +1820$, and $\Delta H = +29,690$. Combining the two equations,



Therefore, since ΔF is here numerically smaller than ΔH , dissociation into *gaseous* sulphur and hydrogen should become appreciable at some temperature.

This equilibrium was the basis of the calculation of the free energy of hydrogen sulphide at high temperature, and the value at 25° C. was calculated³ from this by means of an equation of the type shown on page 45, taking full account of the heat capacities (and their variation with temperature) of the substances concerned—fuller account, in actual fact, than there is experimental evidence for, as the heat capacity of gaseous sulphur is unknown and was *assumed* to be represented by the same equation as is employed for oxygen. An example of the magnitude of the error introduced by neglecting heat capacities and assuming ΔH constant is offered by recalculating the equilibria at high temperature on this assumption—had we used the same equation as was employed in the derivation the results must, of course, have come correct. If, then, ΔH is assumed constant, $I = +5250/298 = +17.62$, and the temperature at which $K = 1$, $T' = -\Delta H/I = +39,210/17.62 = 2225$. By a slight extrapolation of the experimental data⁴⁹ it is found that $K = 1$ at about 1825, and at 2225 $K = 0.32$ (about). Considering the enormous temperature interval, the approximation is remarkably good.

Example 10.—How far is it possible to generalise about the magnitude of the error involved in assuming ΔH constant?

$$\Delta H_T = \Delta H_{298} + \int_{298}^T \Delta C_p \cdot dT.$$

So far as pure solids and liquids are concerned, ΔC_p is usually practically negligible above 25° C. (Kopp's law). For gases it depends mostly upon the change in the number of molecules resulting from the reaction (cf. Nernst's approximate equation), though the complexity of the molecules is of some significance, especially as between monatomic, diatomic, and polyatomic gases which have, respectively, 3, 5, and 6 degrees of freedom. It is, however, usually fairly small, and unless ΔH is itself small, the proportionate variation of ΔH over a range of temperature that is not very great is not serious. Even for changes of state ΔC_p is rarely large. The partial molecular heat capacities of substances in liquid mixtures are very seldom known, but there is some evidence to suggest that in this case ΔC_p may have significant values.

Some idea of the magnitude of the error involved in any given case may be obtained by assuming that ΔC_p , though not zero, is constant (independent of temperature).

$$\text{Then} \quad \Delta H_T - \Delta H_{298} = \Delta C_p(T - 298)$$

$$d \log_{10} K / dT = (\Delta H_{298} / 4.576T^2) + (\Delta C_p / 4.576T) - (298 \cdot \Delta C_p / 4.576T^2)$$

$$\log_{10} K_T - \log_{10} K_{298} = \frac{\Delta H_{298}}{1364} - \frac{\Delta H_{298}}{4.576T} + \frac{\Delta C_p}{1.987} \log_{10} \frac{T}{298} - \frac{(T - 298)\Delta C_p}{4.576T}.$$

Even when $T = 1000$ the difference in $\log_{10} K_T$ from that obtained when neglecting the last two terms is only $0.112 \cdot \Delta C_p$. Experimental equilibrium data can undoubtedly be represented better by formulæ of the power type,

$$\log_{10} K = - \frac{\Delta H_0}{4.576T} + \frac{a \cdot \log_{10} T}{1.987} + \frac{\frac{1}{2}b \cdot T}{4.576} + \dots - \frac{I}{4.576}$$

(see p. 45),

over the range for which they have been studied, but with this form the coefficients of the successive powers of T are usually opposite in sign, each checking the tendency of the term before to become too dominant as the temperature is increased, and having its own influence kept within bounds by the next higher term. To cover a wide range of temperature several terms are required and, if the data are available only at comparatively

low temperatures, only the lower terms are fixed and on extrapolation to higher temperatures ridiculous results are obtained owing to the last term assuming an undue influence unchecked by higher terms which ought to be present. It may be stated quite generally that no such formula is suitable for extrapolation to higher temperatures than those of the data which it was designed to fit. The simpler formulas, assuming ΔH or ΔC_p to be constant, although they lead to increasing error as the temperature is raised, do not show the same inevitable and total failure on wide extrapolation. Normally, such data as found in the literature has been tested up to about 1500, or even 2000 degrees, but to attempt to apply it at, say, the temperature of the electric arc would be to misuse the figures.

For the most careful work, and for preparing values of ΔF for tabulation, the more elaborate formulæ, properly used, are to be preferred, but when it is a case of calculating the position of a possible equilibrium before undertaking an experimental investigation, or to see whether such an investigation is worth while, it is usually sufficient to assume ΔH or ΔC_p constant. In the latter case,

$$\log_{10} K_T = \log_{10} K_{298} + (\Delta H_{298}/1364) - (\Delta H_{298}/4.576T) + x \cdot \Delta C_p$$

where, from the formula previously given, x has been worked out for various values of T and is given in the following table:—

T.	x .	T.	x .
400	0.008	1200	0.140
600	0.043	1400	0.166
800	0.079	1600	0.190
1000	0.112	1800	0.211

Example 11.—Under what conditions could a maximum or minimum value of an equilibrium constant (varying with temperature) be observed?

$$\frac{d \log_{10} K}{dT} = \frac{dK}{K \cdot dT} = \frac{\Delta H}{4.576T^2}$$

and if K passes through a maximum or minimum dK/dT must change sign so that, since K and T are always positive, ΔH must change sign, being 0 at the temperature of the maximum or

minimum. But $\Delta H = \Delta H_0 + \int_0^T \Delta C_p \cdot dT$, and we have seen that ΔC_p is always finite and never very large. If ΔC_p is, at all temperatures, of opposite sign to ΔH_0 there must be some temperature, T' , at which $\Delta H = 0$, but unless ΔH_0 is very small, or ΔC_p is extraordinarily large, T' is likely to be very high. Again, $\Delta F^\circ = -4.576 \cdot T \cdot \log_{10} K$ and ΔF always varies more rapidly with temperature than does ΔH . Since, by the third law, $\Delta F^\circ_0 = \Delta H_0$ it is quite certain that at T' ΔF° will not have the value 0 and most probable that its value will be, numerically, high. No general proof can be advanced because

$$d\Delta F/dT = -\Delta S = -\Delta S_0 - \int_0^T C_p \cdot d \log_e T$$

and, though at all accessible temperatures the integral must be greater than ΔC_p itself (unless it has changed sign), the influence of ΔS_0 may outweigh this. (For example, in the case of the formation of liquid water from its elements ΔF and ΔH both increase as the temperature rises.) It is, however, clear that it would be entirely fortuitous if ΔS_0 had such a value that ΔF was sufficiently small to give K a value within experimentally demonstrable limits at that temperature for which $\Delta H = 0$.

It is theoretically possible that ΔC_p may change sign at some temperature so that ΔH , after numerically increasing with temperature at first, begins to decrease again, but once more the probability of its actually reaching zero at an accessible temperature is slight owing to the prevalent smallness of ΔC_p . It would also be even less likely that $\log_{10} K$ should be such that the equilibrium was analytically demonstrable. We are thus led to conclude that a maximum or minimum value of demonstrable equilibrium is highly improbable, although not impossible. It has been claimed by Maxted⁵⁰ that the formation of ammonia is a case in point, but his experimental evidence does not appear to have been substantiated by later workers, while his theoretical "proof" consisted in extrapolating a power equation of the type discussed in the last example and this, as explained, can prove nothing. In a text-book Mellor⁵¹ claims a maximum for the equilibrium in the formation of hydrogen iodide, but apparently he has inadvertently combined results in aqueous

solution at low temperatures with those of the gaseous reaction at higher temperatures and, of course, this is inadmissible. Bodenstein's ⁵² data definitely show that there is no such maximum in the gaseous reaction at the temperature suggested. Apparently no unquestioned case is known.

The effect of pressure on chemical affinity is of far less general importance than that of temperature, but is readily calculated, when required, from equation (4) from which, for a reaction, it follows immediately that $d\Delta F = \Delta V \cdot dp$. Only a few examples need be given.

Example 12.—What is the chemical affinity of a reaction between perfect gases at unit concentration?

$p = cRT$, where R retains the numerical value, 1.987, if the concentration, c , is expressed in gram-molecules per litre. Let ΔF be the change in free energy at the pressure p (at which $c = 1$) and ΔF° , as usual, that at the pressure 1 atm. Then

$$\Delta F = \Delta F^\circ + \int_1^p \Delta V \cdot dp.$$

If n_1 gram-molecules of reactants produce n_2 of products, $\Delta V = (n_2 - n_1)V = \Sigma nV$, where V is the volume of one gram-molecule of perfect gas at the pressure p , and

$$\int_1^p \Delta V \cdot dp = \Sigma n \cdot RT \log_e p,$$

so $\Delta F = -RT \log_e K_p + RT \cdot \Sigma n \log_e p$.

But if p'_A, p'_B , etc., denote the partial pressures of the reacting substances in some equilibrium mixture at the same temperature, and c'_A, c'_B , the corresponding equilibrium concentrations,

$$\log_e K_p = \Sigma n \cdot \log_e p' = \Sigma n \cdot \log_e (c'RT)$$

and

$$\begin{aligned} \Delta F &= RT(-\Sigma n \cdot \log_e c' - \Sigma n \cdot \log_e (RT) + \Sigma n \cdot \log_e p) \\ &= -RT \log_e K_c + RT \log_e (p/RT), \end{aligned}$$

but $c = p/RT = 1$ by the terms of the problem, and

$$\log_e (p/RT) = 0,$$

so $\Delta F = -RT \log_e K_c$.

The problem really only required that the conventional standard state should be changed from unit pressure to unit

concentration. In terms of activity this means that we set $a = c$ instead of $a = p$. For imperfect gases the procedure is formally the same as before, only the numerical value of the activity is obtained from the isotherms of the gases and the relation $[a = c]_{\text{lim. } c = 0}$.

Example 13.—What pressure is necessary to lower the melting-point of ice one degree?

The latent heat of fusion of ice is about 79.7 cal. per gram.⁵³ For the reaction, ice = water; taking the latent heat of fusion as constant over this small range, $\Delta F = 79.7 + IT$ cal. per gram. At 273° K. the two are in equilibrium, $\Delta F_{273} = 0$, and $I = -79.7/273 = -0.292$, whence $\Delta F_{272} = +0.292$ cal. per gram = +12.1 c.c. atm. per gram. But this value is for atmospheric pressure only. If the pressure be increased from 1 to $p + 1$ atm.

$$(\Delta F_{272})_p = (\Delta F_{272})_1 + \int_1^{p+1} \Delta V \cdot dp = +12.1 + (\Delta V \times p \text{ c.c. atm.}),$$

if ΔV may be taken as constant. This is very nearly the case, the value being -0.0906 c.c.⁵³ per gram, so that for equilibrium

$$(\Delta F_{272})_p = 0 = 12.1 - 0.0906 \times p \text{ and} \\ p = 12.1/0.0906 = 133 \text{ atm.}$$

Thus, equilibrium will exist between ice and water at -1°C. if the pressure ($p + 1$) is 134 atm.

Example 14.—What is the relation between the osmotic pressure of a solution and the activities of the components?

The partial molecular free energy of the solvent in the solution, $\bar{F}_1$, is less than the molecular free energy of the pure solvent, F_1° , but may be raised to the value of the latter by exerting a sufficient pressure on the solution, the necessary excess pressure being known as the osmotic pressure. Since

$$d\bar{F}_1 = RT \cdot d \log_e a_1 = \bar{V}_1 \cdot dp$$

and, in terms of activities, it is desired to raise a_1 to unity, it is required to find the upper limit, $\pi + 1$, such that

$$\int_1^{\pi+1} \bar{V}_1 \cdot dp = -RT \log_e a_1.$$

When we may regard $\bar{V}_1$ as constant and equal to V_1 , the molecular volume of the pure solvent, which is usually the case in reasonably dilute solution, the integral is simply $V_1 \times \pi$ and, therefore, $\pi = (-RT/V_1) \log_e a_1$. If the heat of solution is negligible, a_1 is dependent only on the composition and not on the temperature, so, in such a case, the osmotic pressure may readily be calculated (at any temperature) if a_1 be known from a freezing-point determination or vapour pressure measurement.

For the solute, in a binary solution, $\log_e a_1 = \int_0^{n_2} -\frac{n_2}{n_1} \cdot d \log_e a_2$
 and on substituting $\pi = \frac{RT}{V_1} \cdot \int_0^{n_2} \frac{n_2}{n_1} \cdot d \log_e a_2$.

The value of the integral must either be obtainable from data which show the whole course of the a_2 — composition curve or from some assumption as to its course. If, for example, when n_1 is kept constant, a_2 is found to be proportional to n_2 ,

$$d \cdot \log_e a_2 = d \cdot \log_e n_2,$$

and $n_2 \cdot d \log_e n_2 = dn_2$, whence $\pi = n_2 RT/n_1 V_1$. This formula was found by Morse⁵⁴ to fit the facts for cane sugar solution up to $n_2 = 1$ (when $n_1 = 55.58$) satisfactorily, and much better than the well-known formula of van't Hoff, $\pi = cRT$.

If the assumption be made that the solution is perfect, i.e. that the activities of the components are proportional to their molar fractions, $a_1 = N_1 = 1 - N_2$, whence

$$\pi = RT(-\log_e (1 - N_2))/V_1.$$

On expanding the logarithmic term into a series

$$\pi = \frac{RT}{V_1} (N_2 + \frac{1}{2} N_2^2 + \frac{1}{3} N_2^3 + \dots).$$

For low values of N_2 this is indistinguishable from the former equation since

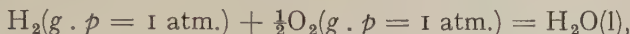
$$n_2/n_1 = N_2/N_1 = N_2/(1 - N_2) = (N_2 + N_2^2 + N_2^3 + \dots).$$

The whole question of osmotic pressure for ideal solutions has been discussed very fully by G. N. Lewis.⁵⁵

Since most inorganic substances in aqueous solution are electrolytes, the relation between free energy and electromotive force, $\Delta F = -nEf$ joules, is of importance.

Example 15.—What would be the electromotive force of the cell, $\text{H}_2(g, p = 1 \text{ atm.})$, $\text{H}_2\text{O}(l)$, $\text{O}_2(g, p = 1 \text{ atm.})$ at 25°C. ?

The reaction of the cell is,



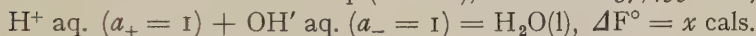
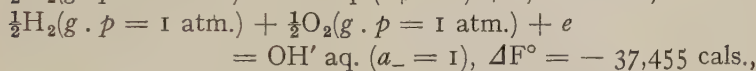
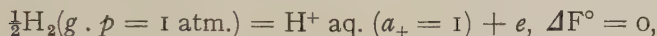
when two faradays pass through the cell. From the table,

$$\Delta F^\circ = -56,560 \text{ cal.} = -236,700 \text{ joules,}$$

$$\text{and } E = +236,700/2 \times 96,500 = +1.227 \text{ volts.}$$

Example 16.—What is the dissociation constant of water at 25°C. ?

The formation of liquid water may also be written as the sum of the three reactions,



the activity of the water being unity, $K = 1/a_+ \times a_-$

$$x + (-37,455) = (-56,560)$$

$$\text{or } x = -19,105 \text{ cal.} = -RT \log_e K.$$

Therefore, $\log_{10} (a_+ \times a_-) = -19,105/1364 = -14.0$. Thus the dissociation constant of water,

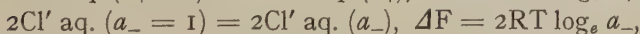
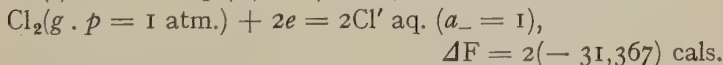
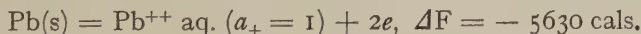
$$a_+ \times a_- = 1 \times 10^{-14} \text{ at } 25^\circ \text{C.}$$

Example 17.—What is the activity coefficient of lead chloride in its saturated aqueous solution at 25°C. ?

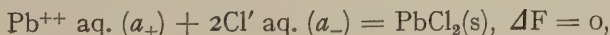
For the reaction,



This may also be written as the sum of the following reactions,



where a_+ and a_- are the activities of the respective ions in the saturated solution, and



since the solid is in equilibrium with the ions in the saturated solution. Summing the free energy changes of this series of reactions and equating to that of the formation of the solid salt,

$$\begin{aligned} RT \log_e (a_+ \times a_-) + 2(-31,367) + (-5630) &= -74,990 \\ \log_{10} (a_+ \times a_-) &= -6626/1364 = -4.858 \\ \log_{10} a_{\pm} &= -1.619 = \bar{2}.381, a_{\pm} = 0.0240. \end{aligned}$$

The solubility is 0.039 gram-molecule per 1000 grams water.⁵⁶

$$\gamma = \sqrt[3]{\left[\frac{a_+}{m} \times \left(\frac{a_-}{2m}\right)^2\right]} = \frac{0.0240}{0.0390 \times \sqrt[3]{4}} = 0.389.$$

This is an unusually low activity coefficient for such comparatively low concentration, but the reason is not far to seek. According to modern theory the concentration of ions in the case of strong electrolytes in dilute solution is equal to their stoichiometrical concentration and the activity is reduced only through the electrostriction prevailing. In such a case the activity coefficient is never very low. With weak electrolytes, however, definite combination of the ions to form undissociated molecules has taken place. The activity is then less than the true molarity of the ion existing as such in the solution because of the effect of electrostriction, but this is small, and the bulk of the difference between the activity and the stoichiometrical molarity is due to the removal of ions as such by combination. Pleissner and Abegg⁵⁷ have shown that the equilibrium



must lie far over on the right-hand side, and it is probable that this reduces the real concentration of lead ions sufficiently to produce unusually low activity coefficients for lead salts.

An interesting case is offered by lead sulphide for which a precisely similar calculation yields $\log_{10} (a_+ \times a_-) = \bar{2}5.73$, $a_+ \times a_- = 5.4 \times 10^{-25}$, and $a_{\pm} = 7.3 \times 10^{-13}$. The solubility has been determined by Hevesey and Paneth,⁵⁸ using lead sulphide in which some of the lead was replaced by its isotope, radium D, and measuring the radioactivity of the saturated solution. In pure water the value found was 1.25×10^{-6} gram-molecules per litre, from which the activity coefficient is about 6×10^{-7} .

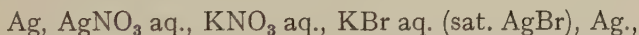
A very low value is to be expected from the effects of

hydrolysis. In very dilute solution activities probably approximate to "true" concentrations, and Knox⁵⁹ found

$$[\text{H}^+][\text{S}''] = 1.2 \times 10^{-15} \cdot [\text{HS}']$$

(where the symbol in square brackets denotes the "true" concentration of the corresponding molecular or ionic species). It follows that in neutral solution ($[\text{H}^+] = 1 \times 10^{-7}$) there should be 1×10^8 times as much sulphur present in the form HS' as in the form S'' and from this cause alone $a_{\text{S}''}/m_{\text{S}} = \gamma_{\text{S}''}$ would be of the order of 10^{-8} . The precipitation data of Noyes and Bray⁶⁰ have been treated in a similar manner by Stieglitz⁶¹ (assuming "true" concentrations equal to activities) and he obtains the value $[\text{Pb}^{++}][\text{S}''] = 1.8 \times 10^{-26}$ as an upper limit, while from experiments of his own he finds the still lower value 2×10^{-27} . If all the data were correct and the assumptions involved in this method of treatment were valid, these numbers should equal $a_{\text{Pb}^{++}} \times a_{\text{S}''}$. There are, however, many uncertainties in calculating "true" concentrations in such a case, and the agreement is perhaps as good as could be expected. On the other hand, with the same assumptions, the activity coefficient, though low, should be considerably higher than the value found above. It is, perhaps, possible that some sulphide was present in colloidal solution in the experiments on the solubility. In any case, the example serves as a warning against assuming activity to be approximately equal to stoichiometrical concentration even at the greatest dilutions without thought for possible disturbing chemical influences.

In passing, the theory of the well-known electrometric method of measuring solubility may be mentioned. In such a cell as



if the liquid junction potentials are negligible or a suitable correction is made for them, the total electromotive force is equal to the sum of the separate electrode effects,

$$E = E^\circ - (RT/f) \log_e a' - \{E^\circ - (RT/f) \log_e a\} = \frac{RT}{f} \log_e \frac{a'}{a},$$

(f denotes the faraday = 96,500 constants).

where a' and a are, respectively, the activities of the silver ion in the nitrate and bromide solutions. If the former is assumed

to be known from the properties of silver nitrate solution and its concentration, the total electromotive force is measured, and therefore, a can be calculated. The activity of the bromide ion in the bromide solution must be practically the same as if it were pure, since the silver bromide is only slightly soluble, and therefore is assumed to be known, whence the product

$$a_{\text{Ag}} \times a_{\text{Br}} = K \times a_{\text{AgBr}}$$

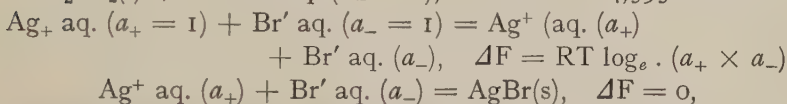
is known. Since the activity of the silver bromide must always be the same when in equilibrium with the pure solid salt (temperature, of course, being constant) the product of the activities of the two ions, called the solubility product, is also constant for all solutions saturated with silver bromide. For a saturated solution of silver bromide alone the activity of each ion may be taken without appreciable error as equal to its concentration, and the solubility is equal to the square root of the solubility product. Measurements of the solubility of silver bromide have been made in this way by Goodwin⁶² and by Thiel⁶³ who obtained, respectively, 6.6×10^{-7} and 8.1×10^{-7} gram-molecules per litre at 25° C. In common with most determinations of solubility by this method, however, the activity coefficients adopted for the silver ion in the silver nitrate and bromide ion in the potassium bromide solutions were not those obtainable by the thermodynamic methods discussed in the fourth chapter, but were the values of λ_v/λ_0 which, at one time, were supposed to afford a measure of what is now called the activity coefficient. The difference is probably not more than about 10 per cent., which is of no great account in solubility measurements, but the whole viewpoint is somewhat different, so no numerical example is here presented. It must be remembered that the activity coefficients discussed in Chapter IV. are the geometric mean of the activity coefficients of the individual ions, and as there is definite evidence that, in general, the separate values of γ_+ and γ_- are not equal, they cannot be obtained by those methods alone. Their determination is to a large extent an unsolved problem, although Lewis³ has taken a considerable step towards a solution, but a discussion of what has been done lies outside the scope of a volume of these dimensions.

From the solubility of an inorganic salt, provided that the activity coefficient in the saturated solution is known or may be

assumed, the free energy of formation of the solid salt may be calculated by the aid of the free energies of formation of the individual ions at unit activity as given in the table.

Example 18.—What is the chemical affinity of silver for liquid bromine forming solid silver bromide at 25° C. ?

The reaction, $\text{Ag(s)} + \frac{1}{2}\text{Br}_2(\text{l}) = \text{AgBr(s)}$, $\Delta F = x$ may be written as the sum of the reactions,



where a_+ and a_- are the activities of the two ions in the saturated solution and may be taken, without sensible error, as being each equal to the solubility. From the electrometric measurements already discussed and the conductimetric measurements of Kohlrausch and Dolezalek,⁶⁴ the solubility is 7×10^{-7} gram-molecules per litre, whence

$$RT \log_e (a_+ \times a_-) = - 16,790 \text{ cal.}, \text{ and } x = - 22,937 \text{ cal.}$$

The chemical affinity is therefore + 22,937 cal.

Whereas with electrolytes the activity coefficients are not known, in general, except for dilute solutions, organic substances frequently form solutions so nearly ideal that the activity of each component may be taken as equal to its molar fraction without appreciable error. This makes the pure *liquid* the standard state for each substance. If the temperature at which the solution is studied is below the melting-point of one of the components, A, it follows that, for the reaction $\text{A(l)} = \text{A(s)}$, ΔF has a negative value, x , dependent only on the temperature and the substance concerned. But the difference between the partial molecular free energy of the substance A in the solution and its molecular free energy in the pure liquid state is $RT \log_e N_A$ if the solution be ideal and N_A is its molar fraction. When, therefore, N_A has such a value, N_A' , that $RT \log_e N_A' = x$, the partial molecular free energy of the substance in the solution at which its molar fraction is N_A' is equal to the molecular free energy of the substance A in the solid state, and the two may exist side by side in equilibrium, i.e. the solution is saturated

with respect to the solid. An interesting example of ideal solution is offered by naphthalene picrate, studied by Brown.⁶⁵ Both naphthalene and picric acid form ideal solutions with nitrobenzene, and the compound shows abnormalities which are completely explicable on the assumption that it dissociates, the activity of the compound being equal to its true molar fraction. Thus an equilibrium constant (using molar fractions) could be deduced. By means of this and the relation just deduced, the free energy of formation of naphthalene picrate from naphthalene and picric acid was determined and found to be in good agreement with the values given by Brönsted⁶⁶ from E.M.F. and solubility data.

If different crystalline forms A and B of the same substance are known and N_A , N_B are their respective molar fractions in saturated solution in any given solvent, the free energy change of the reaction $A(s) = B(s)$ is given by $RT \log_e (N_B/N_A)$, provided the solution is ideal. By testing with several solvents it is usually possible to find a series which give concordant results, and these may be taken as correct, since only ideal solutions are likely to agree; those solutions which are not ideal will show specific deviations.

If the form A has a smaller free energy than the form B there can be no uncompensated spontaneous change of A into B at constant temperature, since all spontaneous changes involve a reduction in free energy. The transformation may be brought about at constant temperature, however, by the compensated spontaneous change in the following way. Let one gram-molecule of A dissolve, forming an unsaturated solution. The change is spontaneous, and therefore involves the degradation of energy in the system as a whole, and the (partial) molecular free energy of the substance A is also diminished. Then allow the solvent to evaporate at constant temperature. Since this is also a spontaneous change, it involves a degradation of energy *in the system as a whole*, but the partial molecular free energy of A increases. Owing to chemical resistance not all possible changes take place, and it will often be found that the solution can be concentrated beyond the saturation value, not only of the form A, but of the form B as well. The solution will then be metastable with respect to both forms. On standing, it does not follow that the change involving the maximum degradation

of energy will necessarily be the first to take place; on the contrary, by Ostwald's rule, the form B is the more likely to separate first, although the further change to form A would involve still further degradation of energy. This does not violate thermodynamic laws in the least, since the change has been brought about by the application of external work—in the evaporation of the solvent. Similarly, form A may be dissolved in greater concentration by the application of heat and then, on cooling, it is possible that form B will separate. Thus, the mere calculation that one form is more stable than another does not imply that the more stable form may not be converted into the other, it only requires that external work shall be done upon it in a suitable manner.

Any reaction can be represented as the sum of a series in which the reactants are first decomposed into their elements, and these are then combined again to form the products, and in consequence the free energy change accompanying the formation of each substance from its elements is desirable if the chemical affinity of any reaction is to be calculated. But many cases of equilibrium are known in which the free energy of formation of the substances reacting has not yet been ascertained and, though the applications of such results are more limited, they can be treated in exactly the same manner as has been employed throughout.

Example 19.—Is it possible to hydrolyse silicon tetrafluoride with water vapour at high temperature?

If this question could be answered in the affirmative a convenient method of analysis of silicates would be offered, since it would be possible to treat the substance with aqueous hydrofluoric acid, evaporate, and pass the resulting vapour through a hot tube when all the silicon would be deposited as silica.

By analysis of the distillate from aqueous hydrofluosilicic acid Baur⁶⁷ found for the reaction



the dissociation constants, K_c , 163×10^7 and 5.4×10^7 at, respectively, 104° and 270° C. whence $\log_{10} K_p = 12.449$ at 377° K. and 11.1277 at 543° K. Using the formula

$$d \log_{10} K/d(1/T) = -\Delta H/2.303 \times R,$$

and assuming ΔH to be constant,

$$\frac{12.4490 - 11.1277}{0.002653 - 0.001842} = -\frac{\Delta H}{4.576} = 1629.$$

Employing the formula given on page 110 adapted to the present figures,

$\log_{10} K_{p_T} = \log_{10} K_{p_{377}} + (\Delta H/4.576 \times 377) - (\Delta H/4.576 \times T)$,
substituting in the numerical values,

$$\log_{10} K_{p_T} = 12.4490 - 4.321 + (1629/T) = 8.128 + (1629/T).$$

This is an interesting example of the case when the chemical affinity ($= RT \log_e K_p$) is increasing with temperature (numerically and, in this instance, algebraically also), but so slowly that $\log_{10} K_p$ itself is diminishing. In such a case, if ΔH remains constant, $\log_{10} K_p$ approaches asymptotically to a limiting value, here 8.128, and practically complete reversal of the reaction is not possible. With such high values of the equilibrium constant analytical errors must be expected to be large and, in addition, since ΔH is only -7450 cals. the effect of any difference in the heat capacities may be considerable, so no great reliance can be placed on the exact figures obtained by a wide extrapolation. Nevertheless, the general conclusion, that no practically complete hydrolysis is to be expected at any temperature, is most probably correct. It is true that Jacobson⁶⁸ passed water vapour and silicon tetrafluoride over glass and failed to observe any deposit of silica, from which he concluded that no hydrolysis took place at all in the vapour state, but he worked at comparatively low temperature and failed to realise how small the amount of silica produced should be according to the data. The present writer in some unpublished work repeated Jacobson's experiments in a quartz tube, heated everywhere to such a temperature that no water condensed and in one part to the full temperature obtainable with a mékka burner. In the comparatively cool parts of the tube no deposit was visible, but in the hot part a very dense deposit was obtained. This completely confirms the calculation made from Baur's data, as it was also found impossible to remove the silicon tetrafluoride from the vapour completely.

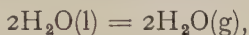
We may now consider an example of a case where the molecular free energy of formation of some of the reacting substances is unknown and recourse is had to the approximation formula of Nernst.

Example 20.—At what temperature will the vapour pressure of water in equilibrium with a mixture of penta- and tri-hydrate of copper sulphate be equal to one atmosphere?

The heat evolved in the reaction



is 5560 cal. according to Thomsen,⁶⁹ and for the reaction



at 25° C., 20,900³ cal. are absorbed, hence for



$$\Delta H = -26,460 \text{ cal.}$$

$K = p_{\text{H}_2\text{O}}^2$ since the activities of the solids are unity, and the increase in the number of gaseous molecules is two. The chemical constant of water is 3.6. Hence, by equation 92,

$$2 \log_{10} p_{\text{H}_2\text{O}} = (-26,460/4.576T) + 2(1.75 \log_{10} T) + (2 \times 3.6)$$

$$\log_{10} p_{\text{H}_2\text{O}} = -2891/T + 1.75 \log_{10} T + 3.6,$$

so, when $p_{\text{H}_2\text{O}} = 1$, $2891/T' = 1.75 \log_{10} T' + 3.6$, where T' is the temperature at which $p_{\text{H}_2\text{O}} = 1$. Solving by trial and error, which is easy, since $1.75 \log_{10} T$ varies but slowly with T ,

$$T' = 359^\circ \text{ K.}$$

It happens that this system has been examined by Lescoeur,¹⁴ and by a slight extrapolation of his figures we find $T'_{\text{ex.}} = 375^\circ \text{ K.}$, while at 359° K. the vapour pressure is 0.403 atm. The vapour pressure is altering very rapidly with temperature in this region, so that the error appears larger when the vapour pressure is calculated for a given temperature than when the temperature at which a given vapour pressure is reached is estimated.

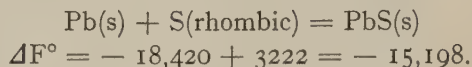
Sometimes the required data exist in the literature in some other form and merely require a little calculation.

Example 21.—What is the standard free energy of formation of lead sulphide?

The entropy difference between lead sulphide on the one hand and metallic lead and rhombic sulphur on the other has

been determined by Rolla ⁷⁰ from measurements of specific heats and a theoretical formula supported by them. (His notation is different, U and A are equivalent, respectively, to $-\Delta H$ and $-\Delta F$ in the notation of Lewis here employed.) At 291° K. he gives, $T \cdot \Delta S = -1611$ cal. per gram equivalent $= -3222$ cal. per gram-molecule.

For the heat of formation of lead sulphide from metallic lead and rhombic sulphur Thomsen ⁶⁹ gives 18,420 cal. per gram-molecule. From equation (3), $\Delta F = \Delta H - T \cdot \Delta S$, and for the reaction,



Again, by equation (6), $d(\Delta F) = -\Delta S \cdot dT$,

and the entropy difference may be taken as constant over a small temperature interval. Accordingly,

$$\Delta F_{298} = \Delta F_{291} + \frac{3222}{291} \times 7 = -15,198 + 77 = -15,275 \text{ cal.}$$

per gram-molecule.

The value of ΔF° for silver sulphide given in the tables is similarly calculated from Rolla's value at 291° K.,

$$U - A = -\Delta H + \Delta F = -T \cdot \Delta S = +521 \text{ cal.}$$

per gram equivalent, and Thomsen's value of the heat of formation ($-\Delta H$) = 3330 cal. per gram-molecule.

APPENDICES.

USEFUL NUMERICAL DATA.

	Logarithm.
$\text{Log}_e . x = 2.303 \log_{10} x$	0.3623
1 Faraday = 96,500 coulombs	4.9845
1 Joule = 0.2389 cal.	1.3783
1 Litre-atmosphere = 24.20 cal.	1.3838
1 Volt-Faraday = 23,060 cal.	4.3628
R = 1.987 cal. per degree per gram-molecule	0.2982
R = 0.08206 litre-atmosphere per gram-molecule	2.9141
R = 8.315 joules per gram-molecule	0.9199
25° C. = 298.1° K.	2.4743
$2.303 \times 1.987 = 4.576$	0.6605
$2.303 \times 1.987 \times 298.1 = 1364$	3.1348

(Values taken to four significant figures from *International Critical Tables*.)

SUMMARY OF SPECIALLY IMPORTANT EQUATIONS.

Equations which are rigidly true.

	Page.
(1) $Q = \Delta E + \int_1^2 p \cdot dv + w$	18
(1B) $(dQ_r = T \cdot dS = dE + p \cdot dV + dW_r)_{\text{reversible changes}}$	31
(2) $H = E + PV$	32
(3) $F = H - T \cdot S$	33
(3c) $(dW_r = -dF)_{p, T, \text{const.}}$	33
(6) $(dF = -S \cdot dT)_{p, \text{const.}}$	40
(6B) $(d(\Delta F/T) = -\Delta H \cdot dT/T^2)_{p, \text{const.}}$	40
(6c) $(d(\Delta F/T) = +\Delta H \cdot d(1/T))_{p, \text{const.}}$	41
(7) $(d\Delta H = \Delta C_p \cdot dT)_{p, \text{const.}}$	44
(8A) $(n_1 \cdot d\bar{F}_1 + n_2 \cdot d\bar{F}_2 + \dots = 0)_{p, T, \text{const.}}$	54
(9) $(dF \text{ (or } d\bar{F}) = RT \cdot d \log_e a)_{T, \text{const.}}$	55
(10) $\Delta F^\circ = \Delta F - RT(n_R \log_e a_R + n_S \log_e a_S + \dots - n_A \log_e a_A - n_B \log_e a_B - \dots)$	56
(10A) $\Delta F^\circ = -RT \log_e K$	56
(16) $(\Delta S = \int_1^2 C_p \cdot dT/T)_{p, \text{const.}}$	97

Approximate Equations.

	Page.
$(\Delta F = RT \log_e \cdot (p'/p))_{T, \text{const.}}$ for gases	37
$(\Delta F = \Delta H + \Delta T)_{p, \text{const.}}$	42
$\log_e \cdot a_1 = -L\theta/R\theta^2$	58
$d \log_e \cdot a_2 = d\theta/\lambda m$	61
$\log_{10} K = (-\Delta H_0/4.576T) + 1.75 \cdot \Sigma n \cdot \log_{10} T + \Sigma(nC)$ for gases	92
$\log_{10} K = [(\Delta H - \Delta F^\circ_{298})/1364] - (\Delta H/4.576T)$ for gases or solutions	110

The following tables show the free energy at 25° C. of one gram formula weight of each substance in its conventional "standard" state for the state of aggregation indicated, when the gram-molecular free energies of the elements in their conventional "standard" states are taken as zero. The numbers are quoted as given in the literature, and the number of significant figures shown does not indicate the probable error in the value. The heat contents are also given whenever these are implicitly involved in the value for the free energy, i.e. when the third law has been used or the value at 25° C. has been obtained by extrapolation of equilibria data at higher temperature, and in some cases where the author concerned has determined it from the temperature coefficient of the free energy. In other cases, where a choice has to be made from the values given in the literature (i.e. the free energy has been determined from equilibria at 25° C.), the selection has been left to the reader.

Except where otherwise indicated, the figures have been taken from Lewis and Randall, *Thermodynamics and the Free Energy of Chemical Substances* (McGraw-Hill Book Co.), by kind permission of the authors and publishers. It should be remarked that these authors have consistently employed the value $R = 1.9885$ cal. per degree per gram-molecule in preference to the figure 1.987 (taken from *International Critical Tables*) employed here.

INORGANIC COMPOUNDS.

Substance.	ΔF° .	ΔH .
¹ AgBr(s)	— 22937 ⁷¹	—
¹¹ AgCl(s)	— 26187	—
Ag ₂ O(s)	— 2395	— 6940
A ₂ gS(s)	— 2290 ⁷⁰	— 3330 ⁶⁹
Al ₂ O ₃ (s)	— 356300 ⁷²	— 352600 ⁷²
As ₂ O ₃ (s)	— 137300 ⁷³	— 153800 ⁷³
Br ₂ (l)	0	0
Br ₂ (g)	+ 755	+ 7590
Br ₂ (s)	+ 314	— 2580
Br ₂ (aq.)	+ 977	—
HBr(g)	— 12540	— 12100
HBr(aq.)	— 24595	—
HBrO(aq.)	— 19680	—

Substance.	ΔF° .	ΔH .
HBrO ₃ (aq.) . . .	+ 2300	—
CaH ₂ (s) . . .	— 34780	—
CaO(s) . . .	— 145300 ⁷²	— 142450 ⁷²
CaCO ₃ (s) . . .	— 270820 ⁷⁴	— 279300 ⁷⁴
Cl ₂ (g) . . .	0	0
Cl ₂ (l) . . .	+ 1146	—
Cl ₂ (aq.) . . .	+ 1656	—
HCl(g) . . .	— 22692	— 22000
HCl(aq.) . . .	— 31367	—
HClO(aq.) . . .	— 19018	—
HClO ₃ (aq.) . . .	— 250	—
HF(g) . . .	— 31800 ⁷⁵	— 32900 ⁷⁵
Fe ₂ O ₃ (s) . . .	— 178400 ⁷²	— 172000 ⁷²
Fe ₃ O ₄ (s) . . .	— 246800 ⁷²	— 236350 ⁷²
Fe ₃ C(s) . . .	+ 3138 ⁷⁶	+ 19162 ⁷⁶
HgCl(s) . . .	— 25137	—
HgO(s) . . .	— 13808	—
I ₂ (s) . . .	0	0
I ₂ (l) . . .	+ 920	+ 4000
I ₂ (g) . . .	+ 15470	—
I ₂ (aq.) . . .	+ 3926	—
HI(g) . . .	+ 315	+ 6150
HI(aq.) . . .	— 12361	—
HIO(aq.) . . .	— 23170	—
HIO ₃ (aq.) . . .	— 31580	—
MgO(s) . . .	— 13700 ⁷²	— 135000 ⁷²
NiO(s) . . .	— 56500 ⁷⁷	— 54170 ⁷⁷
N ₂ (g) . . .	0	0
NH ₃ (g) . . .	— 3910	— 9650
NH ₃ (l) . . .	— 2620	—
NH ₃ (aq.) . . .	— 6300	—
NH ₄ OH(aq.) . . .	— 62860	—
NO(g) . . .	+ 20850	+ 21600
NOCl(g) . . .	+ 16010	+ 12500
NO ₂ (g) . . .	+ 11920	—
N ₂ O ₄ (g) . . .	+ 22640	—
HNO ₂ (aq.) . . .	— 13070	—
HNO ₃ (aq.) . . .	— 26500	—
HNO ₃ (g) . . .	— 18210	—
O ₂ (g) . . .	0	0
O ₃ (g) . . .	+ 32400	—
H ₂ O(g) . . .	— 54507	— 57820
H ₂ O(l) . . .	— 56560	— 68270
H ₂ O(s) . . .	— 56418	—
H ₂ O ₂ (aq.) . . .	— 31470	—

Substance.	ΔF° .	ΔH .
$H_2O_2(g)$. . . —	24730	— 32640
$H_2O_2(l)$. . . —	28230	—
$H_2O_2(s)$. . . —	31470	—
$PbCl_2(s)$. . . —	74990	—
$PbO(s)$. . . —	45050 ⁷⁸	— 52360 ⁷⁸
$PbS(s)$. . . —	15200 ⁷⁰	— 18420 ⁶⁹
$Sb_2O_3(s)$. . . —	190720 ⁷⁹	—
$S(g)$. . . +	30240	—
$S_2(g)$. . . +	18280	+ 29690
$S_8(g)$. . . +	10000	—
$S_\lambda(l)$. . . +	94	+ 360
$S_{\mu,\lambda}(l)$. . . +	93	—
$S(s. \text{ mono.})$. . . +	18	+ 82
$S(s. \text{ rhom.})$. . .	0	0
$H_2S(g)$. . . —	7840	— 4760
$H_2S(aq.)$. . . —	6490	—
$SO_2(g)$. . . —	69660	— 69000
$SO_2(aq.)$. . . —	69770	—
$H_2SO_3(aq.)$. . . —	126330	—
$SO_2Cl_2(g)$. . . —	71560	—
$SO_3(g)$. . . —	85890	— 22600
$H_2SO_4(aq.)$. . . —	176500	—
$TeO_2(s)$. . . —	64320 ⁸⁰	— 77700 ⁸⁰
$TiCl(s)$. . . —	44164	—
$ZnI_2(s)$. . . —	50985 ⁸¹	— 50760 ⁸¹
$ZnO(s)$. . . —	75930 ⁸²	— 83000 ⁸²

CONVENTIONAL STANDARD FREE ENERGY OF FORMATION OF
INDIVIDUAL IONS.

Cations.

Ag^+ . . . + 18448	Hg_2^{++} . . . + 36854	Rb^+ . . . — 67473
Cd^{++} . . . — 18348	K^+ . . . — 67431	Sn^{++} . . . — 6276
Cu^{++} . . . + 15912	Li^+ . . . — 68248	Tl^+ . . . — 7760
Fe^{++} . . . — 20350	Na^+ . . . — 62588	Zn^{++} . . . — 34984
Fe^{+++} . . . — 3120	NH_4^+ . . . — 18930	
H^+ . . . 0	Pb^{++} . . . — 5630	

Anions.

Br' . . . — 24595	CO_3'' . . . — 125760	OH' . . . — 37455
Br_3' . . . — 25230	CO_3H' . . . — 140000	S'' . . . + 23450
BrO_3' . . . + 2300	I' . . . — 12361	SH' . . . + 2980
Cl' . . . — 31367	I_3' . . . — 12315	SO_3'' . . . — 116680
ClO' . . . — 6500	IO_3' . . . — 31580	SO_3H' . . . — 123920
ClO_3' . . . — 250	NO_2' . . . — 8500	SO_4'' . . . — 176500
CN' . . . + 39370	NO_3' . . . — 26500	S_2O_3'' . . . — 125110 ⁸³
CNO' . . . — 23750		

CARBON COMPOUNDS.

Substance.	ΔF° .	ΔH .
Graphite	0	0
Diamond	+ 390	+ 180
Methane	— 12800	— 18350
Benzene	+ 27100	+ 11700
Carbon monoxide	— 32510	— 26140
„ dioxide	— 94260	— 94240
Carbonic acid (aq.)	— 148810	—
Formic acid (l)	— 84040	—
„ „ (aq.)	— 87920	—
Acetic acid ⁴⁴	— 96600	— 115400
Normal butyric acid ⁴⁴	— 92500	— 125300
Palmitic acid ⁴⁴	— 89000	— 211000
Oxalic acid ⁴⁴	— 167500	— 169600
Carbon oxychloride (g)	— 48770	—
„ oxysulphide (g)	— 39600	—
Urea (s)	— 47280	—
„ (aq.)	— 48840	—
Hydrogen cyanide (g) ⁸⁴	+ 29700	+ 30500
„ „ (l)	+ 28870	—
„ „ (aq.)	+ 27520	—
Cyanogen (C ₂ N ₂)(g)	+ 92000	—
„ iodide (s)	+ 42790	—
Cyanic acid (aq.)	— 29100	—
Methyl alcohol ⁴⁴	— 44500	— 59890
Ethyl alcohol ⁴⁴	— 44000	— 65660
N. propyl alcohol ⁴⁴	— 44100	— 72260
Isopropyl alcohol ⁴⁴	— 47400	— 77500
N. butyl alcohol ⁴⁴	— 44100	— 78770
Tert. butyl alcohol ⁴⁴	— 49900	— 88400
Erythritol ⁴⁴	— 152900	— 214800
Mannitol ⁴⁴	— 226200	— 314900
Dulcitol ⁴⁴	— 228100	— 317200
Glycol ⁴⁴	— 82500	— 111100
Glycerol ⁴⁴	— 116700	— 158600
Ethyl ether ⁴⁴	— 33600	— 66000
Acetone ⁴⁴	— 38000	— 57200
Glucose ⁴⁴	— 219000	— 301100

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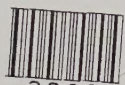
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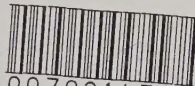
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